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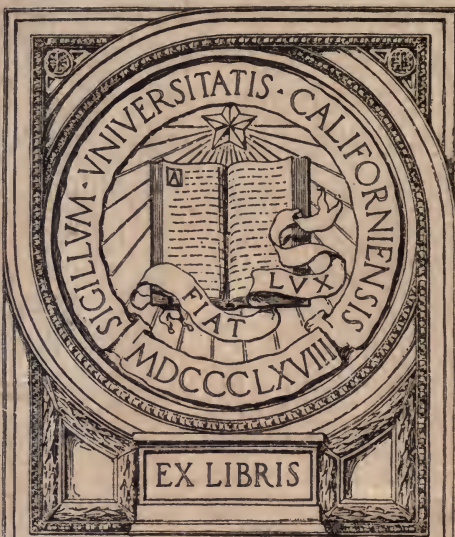
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- I. A Study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential.
- II. The Application of the Hydrogen Electrode to the Measurement of the Hydrolysis of Aniline Hydrochloride, and the Ionization of Acetic Acid in the Presence of Neutral Salts.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY
NATHANIEL EDWARD LOOMIS
BALTIMORE
1911



EASTON, PA.:
ESCHENBACH PRINTING COMPANY

DECLARATION

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Witness my hand and seal this [] day of [] 19[]

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The author also desires to express his gratitude to President Remsen, Professor Morse, Professor Jones and Doctor Swartz for instruction and to Doctor Turner and Doctor Pfund for many valuable suggestions.

A Study of the Hydrogen Electrode, of the Calomel Electrode and of Contact Potential

I. INTRODUCTION.

For several years we organic chemists have felt the need of some direct, very rapid, and accurate method for determining the hydrogen (also hydroxyl) ion concentration of dilute solutions. Such a method would be of special value in the study of many organic reactions involving, for example, the hydrolysis of salts or the saponification of esters, the reactions of addition products in cases of catalysis by hydrogen ions, and many others in which the system is gradually changing.

The methods commonly in use heretofore have presented serious difficulties in their general application. The conductivity method, for example, which has had the widest range

of application, rapidly diminishes in accuracy with increase in dilution of the solution, and furthermore, the measurement of small concentrations of acids in the presence of other electrolytes, especially the salts of these acids with weak bases, is almost impossible. Special methods, such as the use of diazoacetic ester, as suggested by Bredig and Fraenkel,¹ have been used brilliantly in some cases, but are too limited in their range of application. Methods involving titration are of course useless in systems in which a state of equilibrium is established comparatively quickly, for the equilibrium is disturbed as soon as any one of the components is removed.

Although colorimetric methods in the hands of Veley, Salm, Tizard, Szyszkowski and others yield beautiful results in many cases, it has been found that neutral salts affect the colors so greatly in other cases that the method is useless or at least uncertain.

The hydrogen electrode has been recognized by Acree as a possible instrument for the solution of this problem.² Particularly suggestive is the work of H. G. Denham,³ who measured the degree of hydrolysis of several inorganic salts and of aniline hydrochloride. He obtained results agreeing extremely well with those determined by Bredig by the conductivity method. Efforts to duplicate his results and other work on similar lines in this laboratory at first met with serious difficulties, but these are being gradually overcome.

In view of the extreme importance of any favorable results in this field, it seemed worth while to make a careful study of the hydrogen electrode, with special reference to its constancy, the value of its potential in different acids, the ease of reproduction, etc.; in other words, to attempt to make it a standard electrode for use in the same way that calomel and mercurous sulphate electrodes are used. To make the hydrogen electrode an accurate instrument for measuring

¹ Z. Elektrochem., **11**, 525 (1905); Z. physik. Chem., **60**, 202 (1907).

² Desha: Diss., Johns Hopkins Univ., 1909. This work was begun in 1907-8, and reported at the Christmas meeting of the American Association for the Advancement of Science, in 1908. See Science, **30**, 624. Lapworth has also for some time advocated an attempt in this direction.

³ J. Chem. Soc., **93**, 41 (1908).

hydrogen ion concentrations, the measurements must be made with a much higher degree of accuracy than has ordinarily been done.

Early in the investigation it was realized that much of the accuracy of the work would be dependent upon the constancy and ease of reproduction of the calomel electrodes which were used with the hydrogen electrode. For this reason the study of the calomel electrode was gone into very thoroughly.

The method of approaching the problem under consideration resolved itself into five lines of investigation:

1. The study of the relative efficiency of the apparatus used by others and of newer forms devised by me to eliminate various sources of error. The literature and our own experience in this laboratory have shown that there is still much to be done in this line. In this connection I cannot refrain from expressing my deep obligation to Professor H. N. Morse for his kindness in giving me many valuable suggestions when I needed the benefit of the rare knowledge and mechanical skill that have enabled him to overcome such great difficulties in his own researches.

2. The study of the calomel electrodes. A large number of calomel electrodes were prepared and measured against each other so that the value adopted for the potential of the calomel electrode was the average of a number and not dependent upon a single electrode.

3. The preparation of a large number of platinum electrodes which were intercompared by the method used for the calomel electrodes.

4. The direct comparison of the hydrogen electrode with the calomel electrode, involving experiments to determine the efficiency of various solutions in eliminating contact potential.

5. The application of the hydrogen electrode to the determination of the hydrogen ion concentration of various solutions. The hydrolysis of aniline hydrochloride and the effect of neutral salts upon the dissociation of acetic acid were especially studied (see the next part of this dissertation).

II. PREVIOUS WORK

The normal calomel electrode, composed of mercury, calomel and normal potassium chloride solution, was first used and described by Ostwald.¹ It is described as reproducible to within one millivolt. He gives the potential of the electrode as $+0.5600 + 0.0006(t^\circ - 18^\circ)$. This value was determined by Rothmund² by the drop-electrode method.

A year later Coggeshall³ made an extended study of calomel and mercurous sulphate electrodes as to constancy, ease of reproduction, best form of cell, effect of mechanical disturbance, etc. Although this work constituted the most complete study of standard electrodes made up to that time, it left much to be desired. The measurements of potential were made with a Lippman electrometer, which is a far less accurate method than that in which a potentiometer and sensitive galvanometer are used. He did not use the decinormal calomel electrodes at all. Although finding the mercurous sulphate electrodes to be on the whole more suitable for use than the calomel electrodes, he concluded that "bei Anwendung wohl gereinigter Chemikalien und einer Vorkehrung gegen Erschütterungswirkungen, wie eine solche in der partiellen Sandfüllung gegeben ist, sind ohne Mühe Normal-Quecksilber-Kalomel-Electroden herstellbar, deren electromotorische Kraft von dem Normal Wert um nicht mehr als 0.0008 Volt abweicht, und dies mit ausserordentlicher Konstanz."

Smale⁴ was the first to make an extended study of the hydrogen electrode and his work was principally in connection with the oxygen-hydrogen gas element. He concluded that the material (platinum, palladium, gold and carbon) in the electrode used played no part in the electromotive force of the cell, provided that it was not acted upon chemically. The surface and size of the electrodes, above a certain limit, had no effect.

Wilsmore⁵ repeated Smale's work and made allowance for

¹ Ostwald-Luther: "Physiko-Chemische Messungen," 3rd Edition, p. 441.

² Z. physik. Chem., **15**, 15 (1894).

³ *Ibid.*, **17**, 62 (1895).

⁴ *Ibid.*, **14**, 577 (1894).

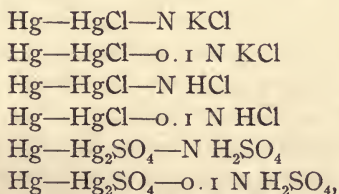
⁵ *Ibid.*, **35**, 296 (1900).

the contact potential of the solutions. In regard to the part played by the electrode, he arrived at the same conclusions as Smale. As his zero of potential he adopted the potential of the hydrogen electrode toward a solution normal with respect to hydrogen ions. On this basis he found the value of the normal calomel electrodes to be 0.283 volt. He calculated the contact potential of a large number of pairs of solutions, using data obtained by others, and studied the electromotive force of the hydrogen-oxygen gas battery and the potential of a large number of metallic electrodes.

Richards¹ found that the temperature coefficients increased with dilution of the solution, and that the decinormal calomel electrode is more uniform in its behavior than the electrodes containing normal potassium chloride solution. He determined the temperature coefficient of the decinormal electrode to be 0.00079. In this work he noticed certain gradual changes in the potential of the calomel cells, especially of those containing the more concentrated salt solutions.

In a later article² Richards and Archibald showed that this gradual change is caused by the formation of a complex mercuric ion by the interaction of the alkali chloride and the calomel. This decomposition is very slightly affected by light or air but is hastened by elevating the temperature or by increasing the concentration of the solution of the alkali chloride. The decomposition is almost negligible in 0.1 N solutions. This work was corroborated by experiments carried on simultaneously by Gewecke.³

Sauer,⁴ in an extended study of various electrodes, including the systems



concluded that the normal potassium chloride-calomel elec-

¹ Z. physik. Chem., **24**, 39 (1897).

² *Ibid.*, **40**, 385 (1902).

³ *Ibid.*, **45**, 685 (1903).

⁴ *Ibid.*, **47**, 146 (1904).

trodes can be made up with a slightly greater degree of uniformity than can the decinormal electrodes, which were found to be reproducible to within about 0.2 millivolt. Light was found to have no effect upon the potential of the calomel electrodes. By direct comparison of the normal and decinormal electrodes he found that if the former is assumed to have a value of 0.560 volt at 18°, the latter will have a value of 0.612.

Sauer's observation as to the greater uniformity of the normal electrodes has been corroborated by Lewis and Sargent,¹ who have also placed emphasis upon the purification of materials and uniform methods of preparation of the calomel-mercury paste.

Palmaer² determined by the drop-electrode method that the absolute potential of the decinormal electrode at 18° is -0.5732 ± 0.0003 . At the same temperature the value of the normal electrode is -0.56 . This gives a difference of 0.013 between the potentials of the normal and decinormal electrodes. By direct comparison Sauer found the difference at 18° to be 0.052. Since the procedure of Sauer is probably a far more accurate method for determining differences in potential than is the drop-electrode method, it has seemed best to adopt Wilsmore's standard as the zero of potential, viz., the potential of the hydrogen electrode toward a solution normal with respect to hydrogen ions. If we use Sauer's value for the difference between the potentials of the normal and decinormal electrodes, the value of the decinormal electrode, according to Wilsmore's standard, becomes $-0.283 - 0.052 = -0.335$ at 18°. At 25° the potential of the decinormal electrode becomes $-0.335 - 0.0008(25^\circ - 18^\circ) = -0.3406$.

Besides the work briefly reviewed above, there has appeared an immense amount of work involving the use of the hydrogen electrode, the calomel electrode or other standard electrodes. In this connection may be mentioned the work of Lorenz and Mohn³ on the neutral point of the hydrogen elec-

¹ J. Am. Chem. Soc., **31**, 362 (1909).

² Z. physik. Chem., **59**, 129 (1907).

³ *Ibid.*, **60**, 422 (1907).

trode; that of Lorenz and Böhi¹ on the electrolytic dissociation of water; that of Lewis and Rupert² on the chlorine electrode; that of Naumann³ on the electromotive force of the hydrogen-cyanogen gas element; that of Schoch⁴ on the oxygen electrode; and many others.

III. THEORETICAL DISCUSSION

The theory of the hydrogen electrode is generally familiar. It will only be recalled here that according to Nernst the potential of the electrode toward the solution in which it is immersed is dependent upon the pressure of the hydrogen gas and upon the osmotic pressure of the hydrogen ions in the solution.

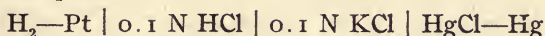
In the comparison of a calomel electrode against a hydrogen electrode in a solution whose hydrogen ion concentration is H' , we find that if π represents the observed electromotive force, π_1 the potential of the calomel electrode against a hydrogen electrode when immersed in a solution with unit concentration of hydrogen ions, and π_2 the contact potential between the solutions of the system, then the equation

$$\pi = \pi_1 - \frac{RT}{F} \log_e H' + \pi_2$$

holds when the hydrogen gas is under atmospheric pressure. From this equation, when $T = (25 + 273^\circ)$ we find that

$$\log_{10} H' = - \frac{\pi - \pi_1 - \pi_2}{0.0591}$$

The value of π is obtained by actual measurement with the potentiometer, π_1 is calculated from some system in which π_2 and $\frac{RT}{F} \log_{10} H'$ are known and π has been previously measured, and π_2 is calculated. The best system for determining the value of π_1 is



in which π can be measured, $\frac{RT}{F} \log_e H' = 0.0591 \times \log_{10}$

¹ Z. physik. Chem., **66**, 733 (1909).

² J. Am. Chem. Soc., **33**, 299 (1911).

³ Z. Elektrochem., **16**, 191 (1910).

⁴ J. Phys. Chem., **14**, 665, 719 (1910).

0.0922, and π_2 can be calculated by some such formula as that of Planck.

Because of the difficulty of calculating π_2 exactly in many cases, attempts have been made to eliminate this potential by interposing between the two solutions in question a saturated solution of some highly soluble salt, the two ions of which have nearly the same migration velocity, such as ammonium nitrate, potassium chloride,¹ and others. The use of ammonium nitrate for this purpose has been advocated by Abegg and Cumming,² who claim that it practically eliminates the contact potential. On this assumption it was used by Denham in his measurements of the hydrolysis of aniline hydrochloride and a number of inorganic salts. That it does not do away entirely with the contact potential was shown by Desha. Some measurements of my own in this connection will be spoken of later.

In order to show a change of 0.1 per cent. in the hydrogen ion concentration of a solution, the measurements must be accurate to within 0.000025 volt, and an accuracy of 0.00001 volt was striven for. The question of the effect of temperature also comes into consideration. Since 1° makes a difference of 0.0008 volt in the potential of the decinormal calomel electrode, the temperature had to be kept constant to within about 0°.01.

IV. EXPERIMENTAL

1. Apparatus

The electromotive force measurements were all made with a Leeds and Northrup potentiometer calibrated by the Bureau of Standards. All measurements were made by the zero method, that is, the potentiometer was adjusted until there was no deflection of the galvanometer. The galvanometer was a Leeds and Northrup special high-sensibility, short-period instrument of the Marvin type. It had a sensibility of 117, a period of 1.7 seconds, and a resistance of 215 ohms.

¹ After this article was in type I learned of the very important work of Bjerrum on the use of a saturated solution of potassium chloride to eliminate contact potential (Z. Elektrochem., **17**, 389; Z. physik. Chem., **53**, 428). His results agree very closely with mine.

² Z. Elektrochem., **13**, 17 (1907).

As primary standards of potential I used two Weston standard cells kindly loaned to me by the Bureau of Standards and calibrated by them from time to time.

The apparatus was tested for leakage currents and thermal effects by making various commutations and found to be free from them within the limit of accuracy of the work. With this apparatus measurements could be made to within 0.00001 volt with a high degree of accuracy. The apparatus was tested by measuring the electromotive force of one standard cell against the other.

Value obtained by Bureau of Standards = 1.01892.

Value measured on the potentiometer = 1.01892.

Value after correcting in accordance with calibration of potentiometer = 1.01892.

The experiments were all carried out at 25° C. The thermometer used in the bath was compared about once a week with a Beckmann thermometer, which was in turn compared to within 0°.002 with two mercury thermometers calibrated by the Bureau of Standards to about 0°.001.

For a constant-temperature bath there was used a glass aquarium 36 × 16 × 15 inches, partially filled with oil, as illustrated in Figs. 1, 7, 7a. At first an attempt was made to use an ordinary water bath, then an oil bath immersed in a water bath, but electric leakage currents in both cases made it necessary to adopt the oil bath. The oil used was a light lubricating oil, very transparent, nearly colorless and odorless, and free from sulphur, as was shown by the mercury test. The heating was accomplished by an electric light, (L) in Fig. 7, which was regulated by a relay and thermoregulator. A fan stirrer situated at one end of the aquarium drove the oil down and under a glass plate placed four inches above the bottom to the further end of the bath, where oil rose and returned through the thermoregulator and above the plate to the stirrer. The glass plate also served as a support for the apparatus used. Under the glass plate is a cooling coil not shown in the figures. The thermoregulator was a toluene grid of the type in use in this laboratory. The temperature regulation was constant to within 0°.01.

The hydrogen used for the hydrogen electrode was generated electrolytically from ten per cent. sodium hydroxide solution, as shown in (*I*), Fig. 7, nickel electrodes being used. A current of about one ampere was generally employed. To remove the last traces of oxygen from the hydrogen, it was passed through an electrically heated tube containing palladium asbestos. The tube (*M* in Fig. 7 and *A* in Fig. 7*a*) was made of Jena combustion tubing, 6 mm. in diameter, and was fitted with a mercury trap at one end. It was covered with a layer of asbestos and inserted in a close fitting brass tube (*N* in Fig. 7) having an inner diameter of 9 mm. Around the brass tube were wrapped 60 ohms of "No. 38 Nichrome" ribbon, the layers being insulated from each other by asbestos paper. When this coil, in series with 73 ohms (a 32 and a 16 c. p. lamp in parallel), was connected to the 110-volt city circuit a temperature of 170° C. was obtained. A slow flow of gas through the tube had no appreciable effect upon the temperature.

From the palladium asbestos tube the hydrogen passed through a washing apparatus (*B*, in Figs. 7 and 7*a*), which contained the same solution as that used around the hydrogen electrode.

The general arrangement of the bath, motor, hydrogen generator and potentiometer is shown in the accompanying photograph, Fig. 1. Since the metallic tank in which the aquarium is placed hides the lower part of the apparatus, a more detailed diagram of it is given later in Fig. 7.

2. Calomel Electrodes

(*a*) *The Preparation of the Materials used in the Calomel Electrodes. Purification of Mercury.*—About thirty pounds of mercury were purified by washing it with 3 per cent. nitric acid for 24 hours in a modified form of Desha's mercury apparatus, illustrated in Fig. 2. In this apparatus three important changes have been made in the form described by Desha. In his apparatus the mercury, descending from the reservoir (*A*), entered a trap and overflowed into the tube

¹ Am. Chem. J., **41**, 152 (1909).

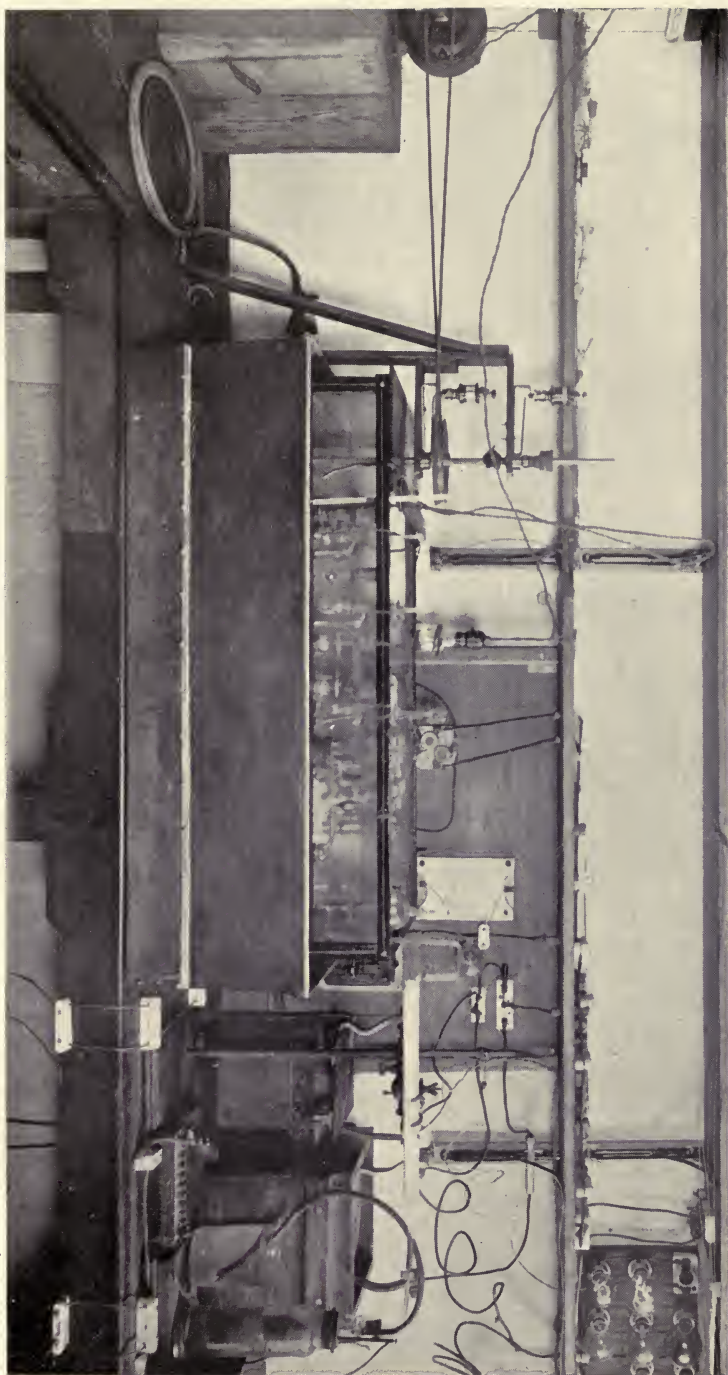
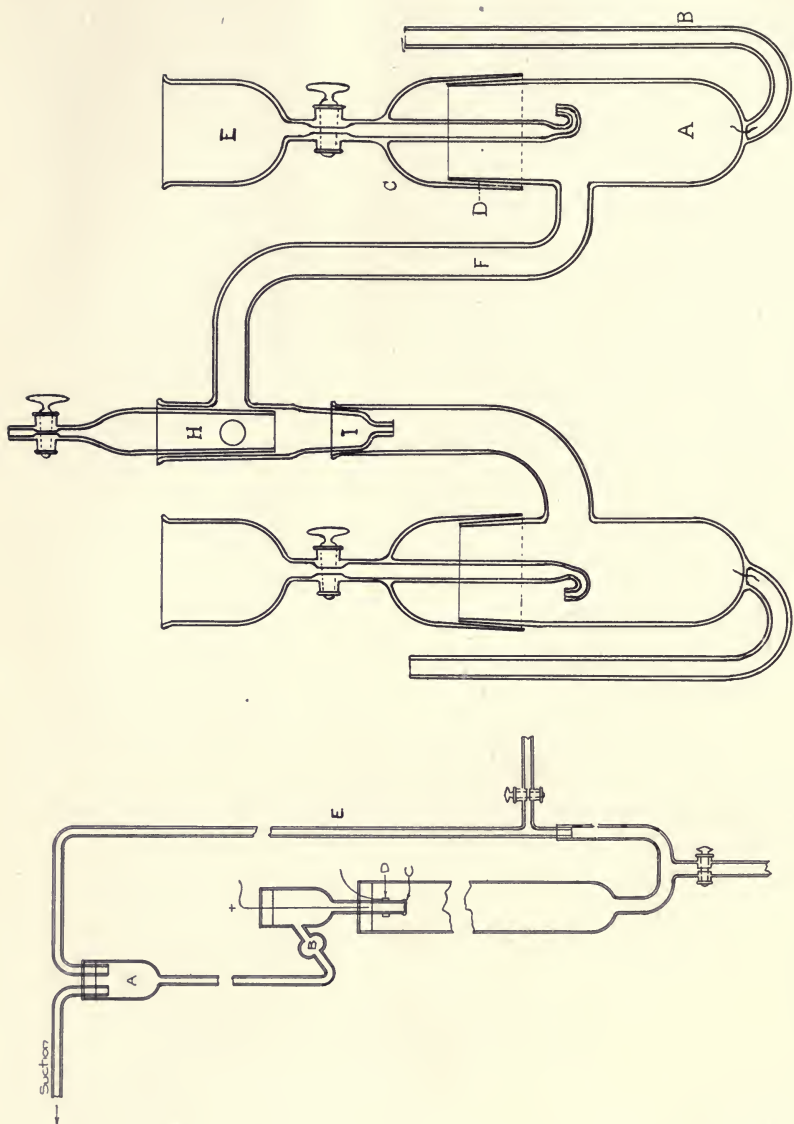


Fig. 1



leading to the nitric acid. This caused a "dead" space which perhaps slightly decreased the efficiency of the washing. In the apparatus shown in the figure this dead space has been eliminated by the substitution of the bulb (*B*), which keeps all the mercury in circulation. A more important change has been made, however, in the method of spraying the mercury into the acid solution. In Desha's apparatus the mercury streamed through holes in a glass bulb. Hildebrand¹ suggested the use of muslin for spraying mercury into acid. Professor Morse and Dr. W. W. Holland in this laboratory have improved upon muslin by using No. 21 bolting silk, which has an extremely fine mesh. This practice has been incorporated in this apparatus, the silk being tied with silk thread to the glass tube at (*C*).

Another change consists in the substitution of a tube (*E*) of 3 mm. internal diameter for the 1 mm. tube which Desha used to draw the mercury from the bottom to the top of the apparatus. This change doubled the rapidity of washing. With the 1 mm. tube three minutes were required for 100 cc. of mercury to circulate through the apparatus; only one and a half minutes are required with a larger tube. This form of apparatus makes possible the electrolysis of the mercury simultaneously with the washing, the column of mercury above the silk being made the anode and a piece of platinum foil introduced at (*D*) the cathode. The platinum cathode was enclosed in a silk bag to prevent the deposited metal from dropping back into the solution. After being washed about 500 times through nitric acid the mercury was rinsed with water and allowed to stand under concentrated sulphuric acid until used.

The mercury thus purified was distilled four times in a current of air in an electrolytically heated Hulett vacuum still. An attempt was made to determine the relative purity of the different samples of mercury by Hulett's² electromotive-force method by using the sample distilled four times as a standard. Although by this method one part of zinc in 10^{10}

¹ J. Am. Chem. Soc., **31**, 933 (1909).

² Phys. Rev., **21**, 388 (1905).

parts of mercury can be detected, no difference could be observed between the samples distilled one, two, three and four times, respectively. I understand that no differences can be detected in the electromotive force of standard Weston cells made in the Bureau of Standards from different samples of mercury purified in a manner similar to mine.

Mercury distilled three times was used for the preparation of calomel and in the calomel electrodes.

Preparation of Calomel.—Pure calomel was prepared by dissolving thrice-distilled mercury in redistilled nitric acid, an excess of mercury being present, then pouring this solution into dilute nitric acid and precipitating the mercurous chloride by the addition of hydrochloric acid with constant stirring. The calomel was filtered and washed thoroughly to remove hydrochloric and nitric acids. It was then shaken with successive portions of water for several days in a shaking machine, then with a dilute solution of potassium chloride and finally with a 0.1 N potassium chloride solution made by dissolving 7.456 grams of ignited recrystallized potassium chloride in conductivity water and diluting the solution to one liter. During the entire procedure free mercury was present and the calomel was protected from the light by the use of bottles painted black.

(b) *Form of Cell.*—Some preliminary experiments were next carried out to determine the relative value of different forms of cells for use in comparing the hydrogen electrode against the calomel electrode. Four different types were used and the one finally decided upon as most efficient and best meeting our requirements is that shown in Fig. 3. The cell consists of a tube (A) about 2 cm. in diameter and 15 cm. high, into the bottom of which is sealed a platinum wire with which contact is made through a side arm (B) containing mercury. Over the top of the cell fits a cap (C) with a ground-glass joint (D). The cap is attached above to a reservoir (E), through which liquid can be poured into the cell. The side tube (F) is about one cm. in diameter. The stopcock (H), in which the side tube of the cell terminates, serves to prevent the diffusion of liquids into the cell. Diffusion is still

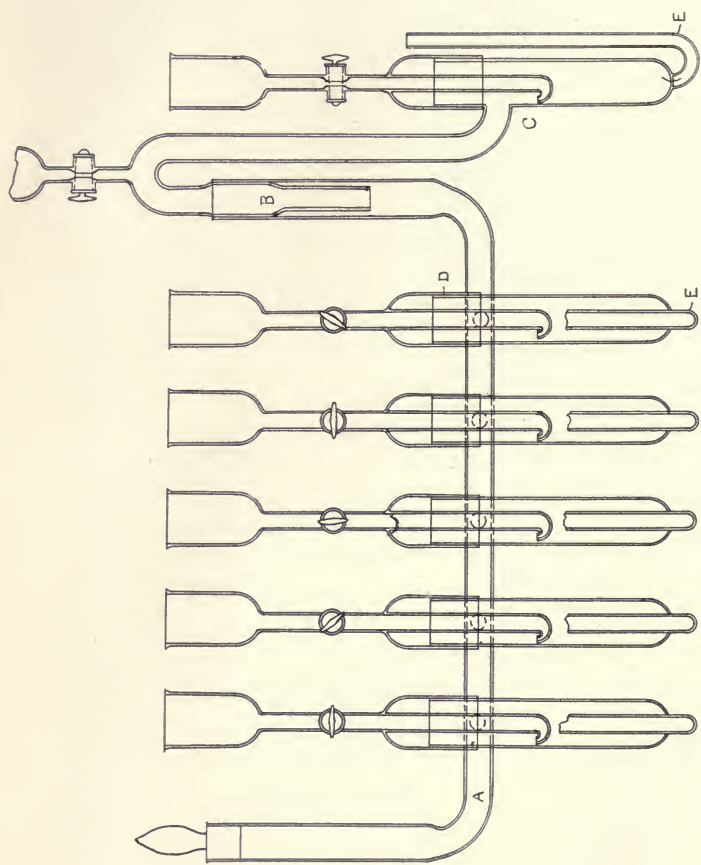


FIGURE 4

more prevented when (*H*) and accessible portions of the wide side tubes are packed with glass or quartz wool. It terminates in the ground joint (*I*) (about 22 mm. long) by which one cell may be connected with another, as shown in the figure, or with the hydrogen electrode apparatus.

The advantages of this form of cell are:

1. The ground-glass cap can readily be removed to allow free access to the inside of the cell for cleaning and filling.
2. The mercury contact through the side arm prevents disturbances of the calomel-mercury paste such as are likely to occur when contact is made by a tube running down inside of the cell.
3. The stopcock and reservoir above the cell permit the rinsing out of the cell with fresh solution when there is any suspicion that impurities have diffused into the side tube.
4. The stopcock at the end of the side tube in a great measure prevents diffusion.
5. The large diameter of the side tube gives a low resistance to the cell.
6. The cell can be immersed entirely in the oil bath, only the reservoirs and stopcocks being above the oil.

This was the form of cell adopted for comparison with the hydrogen electrode. In order that the value used for the potential of the standard electrode might not be dependent upon one electrode only, a battery, Figs. 4 and 4a, of ten cells sealed together was prepared, so arranged that the comparison cell could be checked against this battery. These ten cells were of the same type described above except that the side tube was left off and instead five electrodes were sealed to each side of a central tube (*A*). This central tube was turned up at each end and ground to fit the ground joint (*B*) of the electrode (*C*), or (*I*) of the comparison electrode, shown in Fig. 3; the comparison electrode could therefore be directly checked against any of the ten electrodes. Any defective electrode can be emptied, cleaned and refilled at any time without opening the other nine.

(c) *Filling the Cells*.—Before the cells were filled they were first cleaned with chromic acid and then washed thoroughly

with water. The platinum wires in the bottom of the cells were coated with mercury by the electrolysis of mercurous nitrate solution. The cells were then filled with a strong solution of potassium hydroxide, allowed to stand 24 hours, washed with water and treated successively with chromic acid, water for 2 days, a solution of potassium hydroxide for 12 hours, dilute nitric acid for 2 hours, water and finally alcohol.

In making up the cells the side arms (*E*) were first filled with mercury, that washed in nitric acid being used for this purpose. About 2 cc. of the mercury distilled 3 times was then placed in the bottom of each cell and on top of this about 4 cc. of the calomel-mercury paste. The apparatus was then filled with a decinormal potassium chloride solution previously saturated with calomel. Recrystallized and ignited potassium chloride and conductivity water were used.

In the earlier experiments thick stopcock grease was used for the ground-glass joint (*D*) between the cap and the cell. The cells were then painted over entirely with a black varnish, especial care being taken to get a good coating of paint over the exposed edge of the ground-glass joint. The paint was intended for the double purpose of protecting the calomel from light and of preventing the oil from dissolving the grease in the ground-glass joint. In spite of this precaution considerable difficulty was at first experienced in the creeping of the oil into the cell. Later this difficulty was obviated by the use of sealing wax in the ground-glass joint. This accomplished the purpose desired but was rather inconvenient to use, as the joint had to be heated upon making up or taking down any cell. There was, furthermore, the attendant danger of cracking the apparatus, which, however, never occurred. Another form of joint has been planned which should obviate this difficulty. It is sketched in Fig. 5. It differs from that shown above in having the cap fit into the top of the cell and in having a mercury trap around the base of the joint at (*A*). Sealing wax will be used to close the ground joint at the exposed edge (*B*).

(*d*) *Measurements with the Calomel Electrodes.*—The battery of calomel electrodes was made up 3 times in all. During

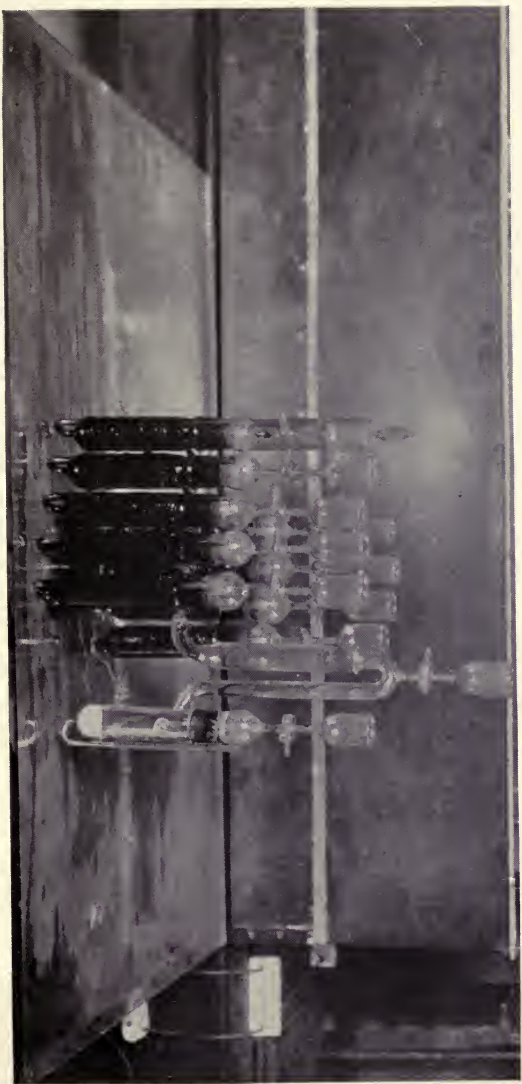


Fig. 4a

the first 2 times difficulty was experienced in keeping the oil out of the cell and individual cells had to be renewed occasionally. The third time sealing wax was used in the joints and this proved efficient in protecting the cell from oil. Only the results of the third series are given in detail. The first 2 series of readings are briefly summarized.

The battery was first made up on November 28, 1910. Four days later the maximum variation of the electrodes was 0.05 millivolt. By December 16, 2 of the 10 electrodes were 0.14 and 0.16 millivolt, respectively, from the mean of the other eight, which differed from each other by a maximum variation of only 0.06 millivolt. These two electrodes were emptied, cleaned out and made up fresh. The potential of these two on December 19 agreed closely with that of the others, there being a maximum variation of 0.10 millivolt. By January 13 the maximum variation had increased to 0.17 millivolt. The battery was taken apart and traces of oil were found in all the electrodes.

The battery was made up a second time on January 24, 1911. On January 26 there was a maximum variation of 0.09 millivolt, which increased to 0.17 by February 10. The caps of the cells were then sealed on with sealing wax. On February 13 the maximum variation was 0.10, which gradually increased to 0.16 by March 7. The battery was then taken apart and cleaned.

On March 9 the battery was made up for the third time and the caps sealed on with sealing wax. In the following tables the calomel electrodes are designated by the numbers 1 to 12. In cleaning the battery Cell No. 6 was accidentally broken and after making up the battery it was found that the potential of No. 7 could not be read because of oil that had crept in between the platinum wire and the mercury in the side tube; only the potentials of 1, 2, 3, 4, 5, 8, 9 and 10 are given. The readings are expressed in hundredths of a millivolt. Cell No. 1 is taken as the standard electrode and considered positive and the potentials of the other electrodes are referred to it. A negative sign before the reading of any electrode means that that electrode is really positive with respect to No. 1.

If, for example, we write No. 1 : No. 9 = +2, No. 9 has a potential of two-hundredths of a millivolt less than No. 1; whereas if we write No. 1 : No. 9 = -2, No. 9 has a potential two-hundredths of a millivolt greater than No. 1.

| Date | | 2 | 3 | 4 | 5 | 8 | 9 | 10 |
|------|----|-----|----|----|---|----|----|-----|
| Mar. | 10 | —11 | 1 | —4 | 6 | —2 | —2 | —23 |
| | 11 | —5 | .. | .. | 9 | .. | .. | —15 |
| | 13 | —4 | 6 | 5 | 7 | 1 | 2 | —2 |
| | 14 | —3 | 7 | 4 | 7 | 1 | 2 | —3 |
| | 15 | —3 | 7 | 5 | 7 | 2 | 3 | —2 |
| | 16 | —2 | 6 | 4 | 6 | 2 | 3 | 0 |
| | 17 | —2 | 5 | 4 | 5 | 0 | 0 | 1 |
| | 18 | —2 | 5 | 2 | 4 | 0 | 0 | 0 |
| | 20 | —5 | 3 | 0 | 1 | 0 | 0 | 1 |
| | 21 | —5 | 2 | 1 | 0 | 0 | —1 | 0 |
| | 22 | —5 | 5 | 0 | 3 | 1 | 1 | 5 |
| | 23 | —5 | 5 | 0 | 2 | 0 | 0 | 4 |
| | 24 | —5 | 3 | 0 | 0 | —4 | —1 | 3 |
| | 25 | —5 | 3 | —3 | 0 | —4 | 0 | 3 |
| | 27 | —1 | 4 | —2 | 0 | —2 | 0 | 5 |
| | 29 | —1 | 0 | —4 | 0 | —5 | 0 | 5 |
| | 30 | —1 | 0 | —6 | 0 | —5 | 0 | 4 |
| | 31 | —1 | 1 | —3 | 4 | —2 | 6 | 7 |
| Apr. | 1 | —3 | 3 | —2 | 4 | —3 | 5 | 5 |
| | 3 | —2 | —1 | —7 | 0 | —7 | 3 | 4 |
| | 4 | 0 | 0 | —4 | 3 | —4 | 4 | 6 |
| | 5 | 0 | 0 | —5 | 3 | —5 | 5 | 5 |
| | 6 | —4 | 0 | —5 | 2 | —6 | 4 | 5 |
| | 7 | —5 | —3 | —7 | 1 | —8 | 3 | 5 |
| | 8 | —4 | 0 | —6 | 1 | —8 | 2 | 5 |
| | 10 | 0 | —2 | —5 | 1 | —5 | 5 | 8 |
| | 11 | 0 | —4 | —5 | 0 | —7 | 5 | 4 |
| | 12 | 0 | —6 | —6 | 1 | —6 | 4 | 3 |
| | 13 | 0 | —4 | —5 | 3 | —6 | 6 | 6 |
| | 15 | 0 | —2 | —4 | 5 | —5 | 7 | 8 |
| | 26 | 0 | 0 | —5 | 3 | —5 | 9 | 10 |
| | 27 | —1 | —4 | —6 | 2 | —7 | 6 | 8 |

| | | | | | | | | 11 (made up) |
|------|----|----|----|-----|---|-----|---|-----------------|
| Apr. | 28 | —1 | —3 | —7 | 1 | —8 | 5 | 5 —13 |
| May | 1 | —2 | —1 | —4 | 2 | —8 | 5 | 5 —6 |
| | 2 | —2 | —3 | —6 | 1 | —9 | 5 | 5 —8 |
| | 3 | —2 | —3 | —6 | 1 | —8 | 5 | 5 —7 |
| | 4 | —2 | —3 | —10 | 0 | —10 | 2 | 5 —6 |
| | 5 | —2 | —4 | —12 | 1 | —11 | 3 | 5 —7 |
| | 6 | 0 | —4 | —11 | 1 | —10 | 3 | 5 —5 |
| | 8 | 0 | —1 | —9 | 3 | —7 | 6 | 10 —1 |
| | 9 | 3 | 0 | —5 | 4 | —4 | 7 | 11 0 |

(e) *Conclusions Regarding the Electrodes 0.1 N KCl-HgCl-Hg.*—An examination of this series of readings shows that decinormal calomel electrodes can be prepared which after the first 4 or 5 days will vary from each other by not more than a tenth of a millivolt, the majority being in even much closer agreement. This agreement lasts for about 3 weeks, after which there is a gradual increase in the maximum variation to 0.14 millivolt after 2 months. Essentially the same facts were observed in the first 2 series of readings made when the battery was set up on November 28, 1910, and again on January 24, 1911.

The average constancy of the mean of the seven electrodes is very good. On March 13 the mean potential of the seven was 2.1, on May 9 it was 2.3, when referred to electrode No. 1.

The constancy of the electrodes is shown by their variations from the mean at the beginning and at the end of the experiment:

| Date | 2 | 3 | 4 | 5 | 8 | 9 | 10 | |
|---------|----|----|----|---|----|---|----|---------------------------------------|
| Mar. 13 | —6 | 4 | 3 | 5 | —1 | 0 | —4 | |
| May 9 | 1 | —2 | —7 | 2 | —6 | 5 | 9 | |
| | | | | | | | | |
| | | | | | | | | +7 —6 —10 +3 —5 +5 +13 = Total change |

The average change in the potential of the individual electrodes with respect to the mean potential was 0.07 millivolt in 2 months. That a gradual change in the potential of all the cells did not occur is shown by the fact that Cell No. 11, made up on April 27, agreed so closely with the others.

The average daily change in the potential of the electrodes was very nearly 0.01 millivolt, although larger variations often occurred.

Lewis has emphasized the necessity of preparing the calomel-mercury paste for the calomel electrode under uniform conditions. To test the effect of a different sample of calomel, 2 electrodes were made up from calomel prepared about 6 months before that used in the battery. Before use it was shaken out with fresh 0.1 N potassium chloride solution. No difference in the potential of the electrodes due to the change in material could be detected.

A few experiments were made to test the effect of light on the potential of the electrodes. As a rule the cells were painted black, but when left unpainted and exposed to the electric light of the bath and the diffused light of the room no change in potential could be noticed.

3. *Experiments upon the Constancy and Accuracy of Reproduction of the Hydrogen Electrode*

In the course of the experiments with the hydrogen electrode there were used 19 platinum electrodes designated by the numbers 1 to 19. Of these electrodes three, Nos. 5, 6 and 7, had been prepared by Desha. Nos. 5 and 6 were sheet electrodes of the same style as Nos. 1-4 and 8-19, inclusive. They were made up of sheet platinum, 1 × 2 cm. in size, welded to a piece of platinum wire 1.5 cm. long, which was sealed into the bottom of a glass tube. Contact was made with the electrode by a small quantity of mercury in the bottom of the glass tube. No. 7 was a Cottrell gauze electrode¹ made by weaving together with fine platinum wire the edges of two platinum wire "baskets" from a broken Linneman fractionating column. This gauze sphere was sealed to the end of a piece of glass tubing, through which the hydrogen passed from the washing apparatus. Contact was made with this electrode by a platinum wire running through the tube of the mercury trap of the washing apparatus. Desha had coated the platinum gauze with gold and then with iridium.²

¹ Robertson: J. Phys. Chem., **11**, 437. Schmidt and Finger: *Ibid.*, **12**, 406.

² Ostwald-Luther, p. 438. Cottrell, Lewis: private communications.

I first used 4 sheet platinum electrodes, Nos. 1-4, inclusive. After the electrodes had been thoroughly cleaned, they were platinized with a solution made of very pure platinum chloride obtained from Heraeus and quite free from iridium and other metals, which often occur in platinum chloride. Electrodes 5, 6, and 7 were also replatinized at this time with the same solution. In platinizing the electrodes no special precautions were used. A potential of 2.5 volts was generally employed and the electrodes adjusted until there was a fairly rapid evolution of gas. The current was commutated each 5 minutes until a good coating of platinum black had been deposited. The behavior of the electrodes appeared to be independent of the thickness of the platinum coating, provided it was so thick that the electrodes did not appear gray.

When platinized, the electrodes were washed with water and then connected 1.5 hours as cathodes in the electrolysis of dilute sulphuric acid. They were finally boiled several hours in water and were then ready for use.

In the earlier experiments the following arrangement was used for comparing the electrodes: Several electrodes were passed through a rubber stopper which fitted the outer jacket of a freezing-point apparatus, and this tube was filled with the acid solution until the electrodes were about three-fourths immersed. The hydrogen was introduced into the solution through a central tube drawn out to a capillary. By this arrangement the hydrogen could not be bubbled directly against the electrodes and hence they were rather slow in coming to equilibrium. The gauze electrode No. 7 could not be compared with the others as its shape prevented its introduction through the rubber stopper. It could be compared with any one of the other electrodes, however, and numerous experiments proved it to have approximately the same potential. These measurements with the gauze electrode are discussed in the next two sections of the experimental work.

In this preliminary work two comparisons of Electrodes 1, 2, 3, 5 and 6 were made. In each case 0.1 N hydrochloric acid was used as the electrolyte. In the first experiment

the electrodes reached a constant potential after 24 hours. Four of the five electrodes showed a maximum variation from each other of 0.08 millivolt. Electrode 1, however, varied by 0.19 millivolt from the mean of the others. It was found to be oily, so it was washed with ether, alcohol and water and then replatinized with pure platinum chloride. After cleaning it thoroughly we compared the electrodes.

In the second comparison the electrodes became constant in potential after 28 hours. The maximum variation between any two was 0.11 millivolt. Four of the five electrodes were within 0.02 millivolt of each other.

Twelve new sheet-electrodes were obtained and were designated by the numbers 8-19. Nos. 8, 9, 12 and 13 were platinized with the pure platinum chloride used for the first electrodes; Nos. 14, 15, 16 and 17 were platinized with ordinary platinum chloride; Nos. 10 and 11 were platinized first with pure platinum chloride and then with the ordinary material, and Nos. 18 and 19 were left bright.

In the comparison of these electrodes another form of apparatus¹ was used. This is shown in Fig. 6. In the actual comparison only one-half of the apparatus was employed. When the second half was used it contained acid of another strength for the comparison of the potentials of the electrodes in acid solutions of two different strengths. The bore of the ground joint (A) which joins the two parts of the apparatus was made of the same size as that used in the pair of calomel cells shown in Fig. 3, so that the hydrogen electrodes might be measured directly against a calomel electrode. The large tubes (B) had an inner diameter of 2.25 inches and were 6 inches deep. This size enabled us to compare readily 8 or more platinum electrodes (D) with each other. The hydrogen bubbled in through the small side tubes (C), and escaped through the tube (E), which was bent downward at the top to prevent the rapid diffusion of air back into the cell.

¹ I have never noticed any ill effects resulting from the use of rubber stoppers in this cell. It was found to be impossible to construct a glass stopper of this size capable of holding a number of platinum electrodes, but I have now devised another type of apparatus in which the rubber stopper is absent. Comparisons will show whether the rubber stopper is objectionable. I can now compare 34 hydrogen electrodes at once.

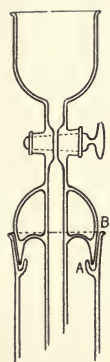


Fig. 5.

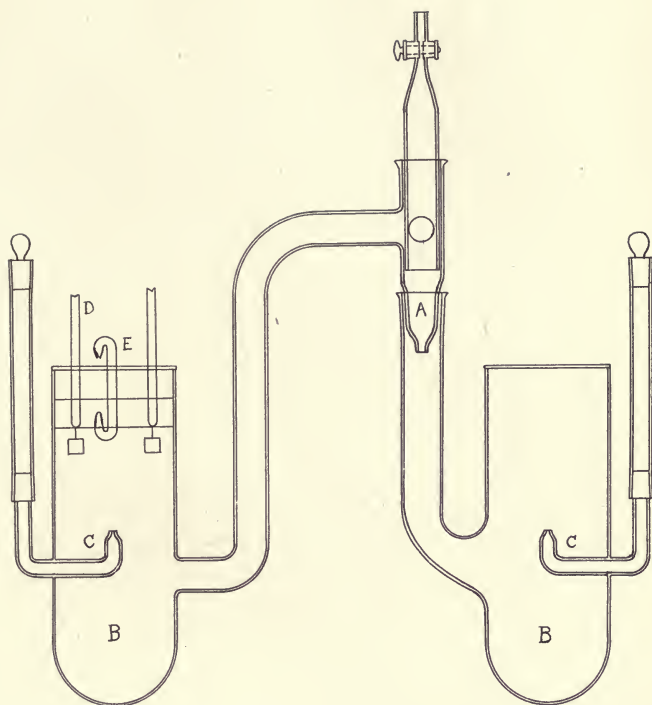


FIGURE 6

Comparison of the Electrodes.—The new electrodes, Nos. 8–17, were not electrolyzed in sulphuric acid before comparison. They were merely washed thoroughly with water and then with alcohol and ether to remove any grease or oil.

In the first experiment Electrodes Nos. 2, 3, 6, 12, 13, 16 and 17 were compared with each other. The detailed measurements are given in the following table. All the electrodes were completely immersed in 0.1 N hydrochloric acid. No. 3 was taken as the comparison electrode and considered positive and the readings with it are given in the same way as in the comparison of the calomel electrodes. The readings are expressed in hundredths of a millivolt:

| Time | 2 | 6 | 12 | 13 | 16 | 17 |
|---------------------|---------|------|-----|-----|----|----|
| May 10, 10.30 A. M. | Started | | | | | |
| 1.00 P. M. | —8 | —637 | —12 | —18 | —1 | —1 |
| 2.00 P. M. | —4 | —272 | —9 | —13 | —1 | —3 |
| 4.00 P. M. | —6 | —160 | —10 | —13 | 1 | 0 |
| 5.00 P. M. | —6 | —109 | —9 | —10 | 0 | —3 |
| May 11, 9.00 A. M. | —1 | —17 | —7 | —7 | 1 | 1 |
| 10.00 A. M. | —1 | —10 | —5 | —5 | —1 | 1 |

The potentials of six of the seven electrodes show a maximum variation of 0.06 millivolt. The maximum variation of any electrode from the mean of all the electrodes is 0.07 millivolt; the average variation from the mean is 0.03 millivolt.

In the second experiment electrodes Nos. 1, 5, 8, 9, 10, 11, 14 and 15 were compared with each other. No. 5 is taken as the comparison electrode. The data of the experiment are given in the following table:

| Time | 1 | 8 | 9 | 10 | 11 | 14 | 15 |
|---------------------|---------|-----|-----|-----|----|------|-----|
| May 12, 11.50 A. M. | Started | | | | | | |
| 1.45 P. M. | —170 | —15 | —21 | —14 | 6 | —347 | —75 |
| 2.30 P. M. | —98 | —10 | —14 | 5 | 6 | —153 | —9 |
| 3.40 P. M. | —36 | —4 | —4 | 2 | 3 | —68 | —3 |
| 4.40 P. M. | —28 | —2 | —2 | 3 | 3 | —52 | 0 |
| 9.00 P. M. | —2 | 0 | 0 | —1 | 0 | —8 | 0 |
| May 13, 9.30 A. M. | —3 | 0 | 0 | —2 | 0 | —17 | —1 |
| 12.30 P. M. | 2 | 2 | 2 | 0 | 1 | —2 | —2 |
| 3.45 P. M. | 3 | 3 | 3 | 3 | 3 | —3 | 3 |

The maximum variation between any two electrodes is 0.06 millivolt. The maximum variation of any electrode from the mean of all the electrodes is 0.05 millivolt, and the average variation from the mean is 0.02 millivolt.

In one of the earlier experiments Nos. 3 and 5 were found to have exactly the same potential. We can therefore reduce all the results of the two above tables to the potentials which should be given when electrode No. 3 is compared against any of the electrodes. Considering No. 3 positive, we obtain the figures:¹

| 1 | 2 | 5 | 6 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|---|----|---|-----|---|---|----|----|----|----|----|----|----|----|
| 3 | -1 | 0 | -10 | 3 | 3 | 3 | 3 | -5 | -5 | -3 | 3 | -1 | 1 |

The maximum variation of any electrode from the mean is 0.095 millivolt. The mean variation from the mean is 0.030 millivolt. I shall try the experiment of connecting different electrodes as cells, or passing a current through them, to see if the potentials can be made more nearly equal.

The experiments show that the potential of the hydrogen electrode is easily reproduced to within 0.10 millivolt and that the potential which the electrode gives is independent of the purity of the platinum chloride used and the thickness of the coating of platinum black, above a certain limit. To clean the electrode, it need not be used as cathode in the electrolysis of sulphuric acid nor boiled with water; rinsing with ether, alcohol and water is sufficient. The electrodes may be completely immersed in the acid solution into which the hydrogen gas is bubbled.

4. *Comparison of the Hydrogen Electrode with the Calomel Electrode*

Apparatus and Method of Procedure.—The apparatus used in the comparison of the hydrogen electrode with the calomel electrode is shown in Figs. 7 and 7a. The arrangement of the apparatus there is that which was employed when a solu-

¹ In this calculation it is assumed that the relative potentials of Nos. 3 and 5 are constant. This assumption is justified by later experiments in which Electrodes 6 and 7 in different solutions of aniline hydrochloride were found to maintain constant relative potentials. I shall study this point further.

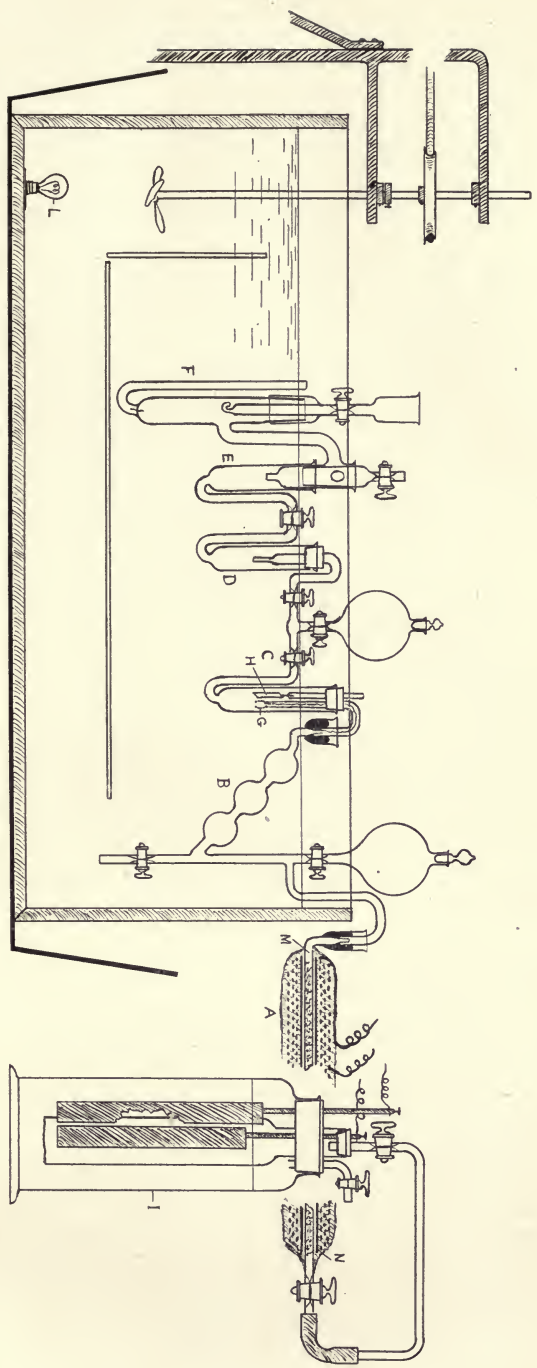


Fig. 7.

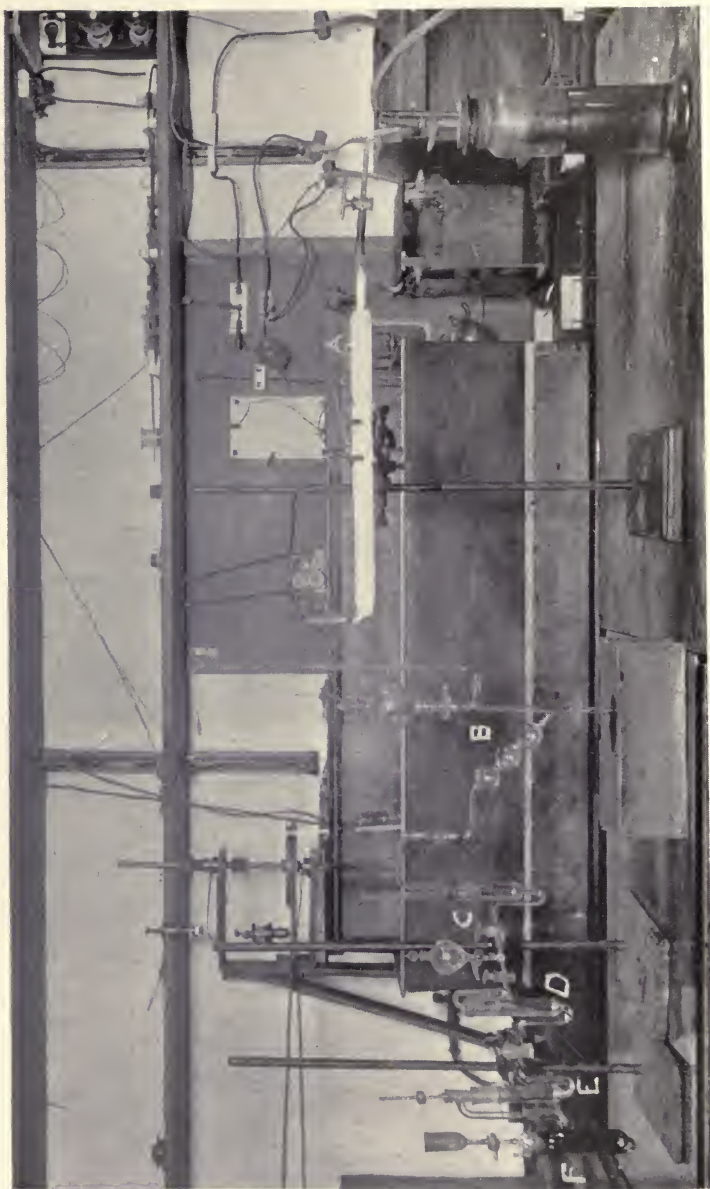


Fig. 7a

tion was used to eliminate the contact potential. The hydrogen passed from the palladium asbestos tube (*A*) through the washing apparatus (*B*) to the gauze electrode (*G*). In most of the experiments a sheet electrode (*H*) was also used, so that one electrode would serve as a check upon the other. The solution in the hydrogen-electrode chamber also filled the rest of the piece of apparatus (*C*). The end of (*C*) dipped into the chamber (*D*) which contained the saturated solution for eliminating contact potential. This solution was prevented from diffusing back into the hydrogen-electrode chamber by the two stopcocks on (*C*). In the chamber (*E*) was placed a 0.1 N solution of potassium chloride the same as that in the calomel cell (*F*). This solution prevented any diffusion into the calomel electrode of the solution for eliminating contact potential.

In the earlier experiments the hydrogen electrode was compared directly with the calomel electrode without the use of any solution for eliminating contact potential. In such experiments chamber (*D*) served as the hydrogen-electrode chamber and potassium chloride solution was put in (*E*). The piece of apparatus (*C*) was not used. The stopcocks were always closed when measurements were not being made, and often even during measurements. The thin film of solution around the stopper served to conduct the current, although under these conditions the measurements were not quite so accurate. This procedure served to stop diffusion and the attendant changes in potential.

After some preliminary experiments the following method of procedure was adopted: The comparison calomel electrode was first compared with the calomel electrodes of the battery and then placed in position for use with the hydrogen electrode. The objection might be raised to this method of procedure, especially in view of the experience of Coggeshall, that the comparison electrode would change in potential by being moved around. To eliminate any such source of error the comparison calomel cell was again compared with the battery at the completion of the experiment. This was hardly necessary, however, as the following experiment to

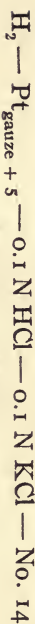
test the effect of mechanical disturbance shows. Cell No. 14, one of the comparison electrodes, gave a voltage against No. 7 of the battery of 0.00029 volt. No. 14 was then moved around and put back again with the battery. The voltage of 14 : 7 was 0.00030, a change of only 0.00001 volt. A still more striking proof of the small effect of mechanical disturbance occurred by accident. On February 3, 14 : 7 gave a voltage of 0.00023. On the morning of February 4 No. 14 fell over in the oil bath, flat on its side. It was quickly picked up, the side tube below the stopcock freed from oil (the stopcock was closed at the time of the accident) and immediately compared with No. 7; 14 : 7 gave a reading of 0.00030, a change of only 0.00007 volt being caused by the accident.

The figures just given show the reason for the method of procedure adopted. Whereas the calomel electrodes in the battery were very nearly constant in value, the potential of the comparison electrode fluctuated from day to day, being generally in the neighborhood of two to three-tenths of a millivolt lower in potential than the cells of the battery. This is to be explained by the constant disturbance this cell was subjected to and also to the likelihood of impurities diffusing into the cell during measurements.

Measurement of the Hydrogen Electrode against the Calomel Electrode.—A typical experiment in which the hydrogen electrode was compared with the calomel electrode is given below. The calomel electrode is positive.

An experiment in which two electrodes were used, covering considerably more time, is given on page 29. The gauze electrode, it will be noted, reaches a constant potential much sooner than the sheet electrode. "No. 14" is the calomel electrode, "5" and "gauze" are the two hydrogen electrodes.

The figures given in the seventh column should theoretically be the difference between those in the third and fifth columns. The comparison of the observed and calculated differences shows the accuracy of the measurements.



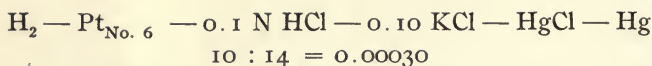
14 : 7 = 0.00030

E. M. F.

| Time Feb. 13 | Bar. pres. in ats. | + — 14 : gauze | | + — 14 : 5 | | + — 5 : gauze | |
|-----------------|-----------------------|-----------------------------|-------------------|-----------------------------|-------------------|------------------|------------------|
| | | Corr. for calomet elect. | Corr. for bar. | Corr. for calomet elect. | Corr. for bar. | Ob- served. | Calcu- lated. |
| 9.00 A. M. | 1.003 | 0.42665 | Started | 0.42604 | | 0.00058 | 0.00061 |
| 10.50 A. M. | | 0.42651 | | 0.42594 | | 0.00054 | 0.00057 |
| 11.33 A. M. | | 0.42650 | | 0.42610 | | 0.00040 | 0.00040 |
| 12.12 P. M. | | 0.42658 | | 0.42618 | | 0.00039 | 0.00040 |
| 12.52 P. M. | | 0.42660 | | 0.42624 | | 0.00038 | 0.00036 |
| 1.58 P. M. | | 0.42652 | | 0.42634 | | 0.00020 | 0.00018 |
| 3.45 P. M. | | 0.42654 | | 0.42645 | | | 0.00009 |
| 4.18 P. M. | | 0.42657 | | 0.42647 | | 0.00009 | 0.00010 |
| 4.40 P. M. | 1.003 | | | | | | |
| Feb. 14 | | | | | | | |
| 8.50 A. M. | 1.0044 | 0.42687 ¹ | 0.42676 | 0.42673 | 0.42662 | 0.00012 | 0.00014 |
| 9.50 A. M. | | 0.42688 | 0.42677 | 0.42680 | 0.42669 | 0.00007 | 0.00008 |
| 11.00 A. M. | | 0.42685 | 0.42674 | 0.42678 | 0.42667 | 0.00006 | 0.00007 |
| | | Stopped | | | | | |

14 : 7 = 0.00029

¹ In Baltimore we often have large and sudden fluctuations in the barometric pressure. Since the platinum electrode does not come into equilibrium with the gas instantaneously there is often an uncertainty in the value of the true electromotive force, as is illustrated in this experiment. We have now devised a simple piece of apparatus for keeping the pressure constant at any desired value, and this will be used especially in testing the relation of the electromotive force of the hydrogen electrode to the partial pressure of the hydrogen.



| Time | E. M. F. |
|---|----------|
| 10.30 A. M. | Started |
| 20 | 0.4050 |
| 24 | 0.4153 |
| 56 | 0.42547 |
| 11.12 | 0.42590 |
| 38 | 0.42610 |
| 12.03 P. M. | 0.42616 |
| 25 | 0.42619 |
| 31 | 0.42619 |
| 37 | 0.42619 |
| Stopped | |
| Observed E. M. F. | 0.42619 |
| Correction for calomel cell | +0.00030 |
| Barometric pressure, ¹ 0.983 ats.; | |
| bar. correction | +0.00044 |

E. M. F. 0.42693

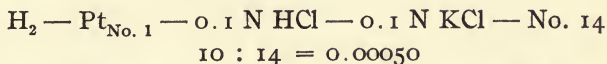
The following table gives the summary of a number of experiments made in this way:

| Pt electrode used | Bar. pres. in ats. | E. M. F. observed | E. M. F. corrected for calomel electrode | E. M. F. corrected for bar. |
|-------------------|--------------------|-------------------|--|-----------------------------|
| "Gauze" | 1.014 | 0.4265 | 0.4266 | 0.42624 |
| No. 5 | 1.014 | 0.4261 | 0.4262 | 0.42584(?) |
| No. 3 | 1.000 | 0.4265 | 0.4266 | 0.42660 |
| No. 2 | 1.000 | 0.4263 | 0.4264 | 0.42640 |
| No. 4 | 1.003 | 0.4266 | 0.4267 | 0.42662 |
| No. 1 | 1.003 | 0.4262 | 0.4267 | 0.42662 |
| No. 6 | 0.983 | 0.4262 | 0.4265 | 0.42694 |
| No. 6 | 1.007 | 0.4266 | 0.4264 | 0.42622 |
| "Gauze" | 1.009 | 0.4272 | 0.4267 | 0.42647 |
| "Gauze" | 1.002 | 0.4269 | 0.4266 | 0.4265 |
| No. 5 | 0.998 | 0.4269 | 0.4266 | 0.42665 |
| "Gauze" | 0.998 | 0.4270 | 0.4267 | 0.42675 |
| "Gauze" | 0.998 | 0.4269 | 0.4266 | 0.42665 |
| No. 5 | 0.998 | 0.4268 | 0.4265 | 0.42655 |
| Average | | | 0.42656 | 0.42652 |

¹ The barometric pressure is given in atmospheres; i. e., 760 mm. at 0° C. and 45° latitude. This does not include a correction of about 23.5 mm. for the vapor tension of the solutions at 25°. This correction seems never to have been made by others. The error involved when barometer readings are referred back to 760 mm. partial pressure of hydrogen, as shown by the data presented in this article, is only about 0.00001 volt for the ordinary pressures.

If the very low value 0.42584 is omitted the average is 0.42657, whether the barometer correction is applied or not. If the value 0.42584 is omitted, the mean deviation of the individual readings from the average is 0.00011, and the maximum deviation is 0.00037. As a working average I shall use 0.4266. This is very close to the value 0.4270 found by Bjerrum.

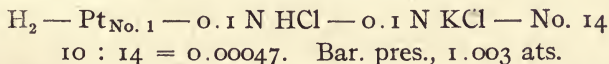
Besides the experiments given above, there were also a few experiments in which values were obtained not agreeing with the others, but in which it was shown that the platinum electrode was at fault.



| Time | E. M. F. |
|-------------------------|----------|
| 1.00 P. M. | Started |
| 2.24 | 0.3666 |
| 2.36 P. M. | 0.3675 |
| Electrode moved | |
| 2.38 P. M. | 0.3666 |
| 2.41 P. M. | 0.3674 |
| 2.44 P. M. | 0.3682 |
| 2.48 P. M. | 0.368 |
| 2.55 P. M. | 0.3694 |
| Electrode turned around | |
| 3.06 P. M. | 0.3659 |
| Experiment stopped | |

On inspection the coating of platinum black was found to be very thin. The electrode was replatinized with pure platinum chloride and electrolyzed in sulphuric acid.

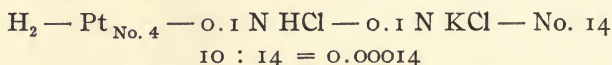
We then repeated the above experiment.



| Time | E. M. F. | Time | E. M. F. |
|-------------|----------|-----------------------------|----------|
| 9.00 A. M. | Started | 11.01 A. M. | 0.42620 |
| 10.08 A. M. | 0.42524 | 11.18 A. M. | 0.42630 |
| 10.13 A. M. | 0.42567 | 11.40 A. M. | 0.42615 |
| 10.23 A. M. | 0.42604 | 0.42615 = obs. E. M. F. | |
| 10.29 A. M. | 0.42615 | +0.00047 = corr. for No. 14 | |
| 10.44 A. M. | 0.42619 | -0.00008 = corr. for bar. | |
| 10.52 A. M. | 0.42620 | 0.42654 = corr. E. M. F. | |

It is seen that the value 0.42654 now given by Electrode No. 1 is in good agreement with the average value of a large number of experiments given above.

In the experimental work dealing with the comparison of the hydrogen electrodes Electrode 4 was broken. In resealing the platinum wire into another piece of glass the platinum black was turned to gray by ignition. This gray electrode was tried in one experiment:



Calomel electrode considered positive

| Time | E. M. F. |
|-------------|----------|
| 9.00 A. M. | Started |
| 10.12 P. M. | 0.00344 |
| 10.16 A. M. | 0.00280 |
| 10.23 A. M. | 0.00240 |
| 10.48 A. M. | 0.00336 |

Stopped

Electrode 4 was now platinized with ordinary platinum chloride solution, electrolyzed in sulphuric acid, washed with water and again used to check the above experiment. This time a value of 0.4267 was obtained.

Discussion of Results.—In the value 0.42657 of the potential difference measured in these experiments are included three factors, the potential of the calomel electrode, the potential of the hydrogen electrode and the contact potential of the two solutions, decinormal hydrochloric acid and decinormal potassium chloride. For calculating the contact potential of two solutions various formulas have been proposed. The first formula was that of Planck.¹ When applied to two solutions having the same concentration this formula becomes

$$\pi_{25^\circ} = 0.059 \log_{10} \frac{u_1 + v_2}{u_2 + v_1}$$

where u_1 , u_2 , v_1 and v_2 represent the migration velocities of the anions and cations of the two solutions. Using the data of Kohlrausch and Holborn we obtain at 25° the values

$$\text{H}^+ = 352.1, \text{K}^+ = 74.5, \text{and } \text{Cl}^- = 75.3$$

¹ Wied. Ann., 40, 561 (1891).

Substituting these data in the equation we obtain 0.0274 as the value of the contact potential at 25°.

There have been various modifications of this formula, for example, that of Henderson¹ and that of Lewis and Sargent.² Bjerrum,³ in a discussion of the accuracy of Planck's and Henderson's formulas, gives 0.0277 as the value of the contact potential between 0.1 N potassium chloride and 0.1 N hydrochloric acid. He also noticed that in the case of some solutions there was a small change in the potential at first, due to diffusion at the planes of contact between the solutions.

Lewis and Sargent's formula has the form

$$\pi = \frac{RT}{F} \log_e \frac{\lambda_1}{\lambda_2}$$

where λ_1 and λ_2 represent the equivalent conductivities of the two solutions. Lewis and Rupert⁴ give the values 389.9 for the equivalent conductivity of 0.1 N hydrochloric acid and 128.8 for 0.1 N potassium chloride. These data substituted in the above equation give 0.0284. The same data when applied to Planck's original formula give 0.0266. In the article by Lewis and Sargent 0.0286 is the value given and further evidence for this value is found in the fact that it is identically the same as the value found by Sauer for the potential difference of the combination



Lewis claims to have ample proof that 0.1 N potassium chloride and 0.1 N hydrochloric acid are equally dissociated (86 per cent.). If the concentration of chlorine ions is the same in each solution, of course the potential of the 0.1 N potassium chloride-calomel electrode will be identical with the potential of the 0.1 N hydrochloric acid-calomel electrode, and the whole

¹ Z. physik. Chem., **59**, 118 (1907); **63**, 325 (1908).

² J. Am. Chem. Soc., **31**, 363 (1909).

³ Z. Elektrochem., **17**, 58 (1911).

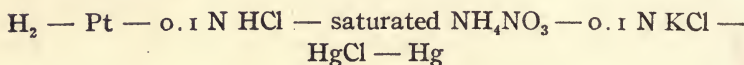
⁴ J. Am. Chem. Soc., **33**, 306 (1911).

difference found in comparing the two electrodes will be due to the contact potential.

We thus see that by the use of different data and formulas the calculated values of the contact potential between 0.1 N hydrochloric acid and 0.1 N potassium chloride vary from 0.0266 to 0.0286. As this difference is much greater than is desirable, it was attempted to use some solution to eliminate the contact potential.

Experiments to Determine the Efficiency of Several Solutions for Eliminating Contact Potential.—Following the suggestion of Abegg and Cumming, ammonium nitrate was first used. In these experiments the arrangement of apparatus was that shown in Fig. 7.

The summary of three experiments with the combination

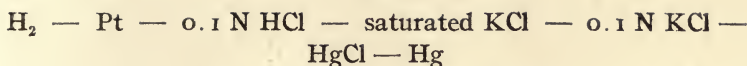


is as follows:

| Experiment | Bar. pres. in ats. | E. M. F. | |
|---------------|-----------------------|-------------------------------|-----------------------------|
| | | Corrected for calomel cell | Corrected for bar. pres. |
| 1 | 0.938 | 0.3990 | 0.39931 |
| 2 | 1.009 | 0.3998 | 0.39957 |
| 3 | 1.002 | 0.3995 | 0.39946 |
| Average value | | 0.3994 | 0.39944 |

The presence of the saturated ammonium nitrate solution causes a difference in electromotive force of 0.4266—0.3994 = 0.0272.

The requisites of a good salt for eliminating contact potential are that it shall be very soluble and that the velocities of the ions shall be nearly equal. Potassium chloride, while not nearly as soluble as ammonium nitrate, has almost identical velocities for its ions. Saturated ammonium nitrate is about 11 N; saturated potassium chloride at 25°, 4.12 N. The effect of 4.12 N potassium chloride solution was next tried. The following table is a summary of the experiments. Two electrodes were used in each case:



| Experiment | Bar. pres. in ats. | E. M. F. | |
|---------------|-----------------------|---------------------------|-----------------------------|
| | | Corrected calomel cell | Corrected for bar. pres. |
| 1 | 1.006 | 0.4002 | 0.40005 |
| | | 0.4002 | 0.40005 |
| 2 | 1.000 | 0.4000 | 0.40000 |
| | | 0.4000 | 0.40000 |
| Average value | | 0.4001 | 0.4000 |

The saturated potassium chloride solution causes a difference of $0.4266 - 0.4000 = 0.0266$ volt.

It was impossible to tell from these experiments whether it was better to use potassium chloride or ammonium nitrate, so a series of experiments was run with different concentrations of acids. Here it was possible to calculate the theoretical difference in the electromotive force due to the known change in hydrogen ion concentration. By comparing this theoretical difference with the observed difference, the relative efficiency of different solutions for eliminating contact potential could be determined. Besides ammonium nitrate and potassium chloride, the effect of potassium iodide, potassium bromide and calcium acetate was determined.

In calculating the hydrogen ion concentration of the hydrochloric acid solutions used the following dissociation values were taken:

| | | |
|-------------|-----------------|--|
| N HCl | 81.0 per cent. | Determined by Sauer |
| .0.1 N HCl | 92.2 per cent. | |
| 0.01 N HCl | 96.9 per cent. | Determined by A. A. Noyes ¹ |
| 0.001 N HCl | 100.0 per cent. | |

The following table summarizes the results:

¹ The Electrical Conductivity of Aqueous Solutions, Carnegie Institution Publication No. 63, page 141.

| Contact soln. | Bar. pres. in at. | HCl conc. | E. M. F. | | Difference | |
|-------------------------------|----------------------|-----------|---------------------------------------|---|------------|--------|
| | | | Corrected for calomel electrode | Corrected for barometric pressure | Obs. | Calc. |
| 11 N NH_4NO_3 | 1.003 | 1.01 N | 0.3364 | 0.33632 | 0.0632 | |
| " | | | 0.3368 | 0.33672 | 0.0628 | 0.0576 |
| " | 1.003 | 0.1006 | 0.3996 | 0.39952 | | |
| " | 1.011 | 0.01006 | 0.4566 | 0.45632 | 0.0568 | 0.0578 |
| " | 1.005 | 0.001006 | 0.4566 | 0.45632 | | |
| 4.12 N KCl | 0.989 | 1.01 | 0.5126 | 0.51247 | 0.0562 | 0.0582 |
| " | | | 0.5126 | 0.51247 | | |
| " | 1.006 | 0.1006 | 0.3418 | 0.34208 | | |
| " | | | 0.3420 | 0.34228 | | |
| " | 1.006 | 0.1006 | 0.4001 ¹ | 0.40000 | 0.0579 | 0.0576 |
| " | 0.997 | 0.01006 | 0.4578 | 0.45788 | 0.0577 | |
| " | | | 0.4578 | 0.45788 | 0.0579 | 0.0578 |
| " | 1.005 | 0.001006 | 0.5162 | 0.51607 | | |
| " | | | 0.5162 | 0.51607 | 0.0582 | 0.0582 |

¹ This is the average of four measurements given on page 31.

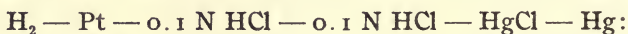
TABLE---(Continued)

37

| | Bar. pres. in ats. | HCl conc. | E. M. F. | | Difference | |
|---|-----------------------|-----------|---------------------------------------|---|------------|--------|
| | | | Corrected for calomel electrode | Corrected for barometric pressure | Obs. | Calc. |
| Contact. soln. 4.3 N Ca(O ₂ CCH ₃) ₂ | 0.998 | 1.01 N | 0.3661 | 0.36615 | 0.0712 | 0.0576 |
| " | 0.998 | 0.1006 | 0.3661 | 0.36615 | | |
| | | | 0.4373 | 0.43735 | | |
| | | | 0.4373 | 0.43735 | 0.0664 | 0.0578 |
| " | 0.991 | 0.01006 | 0.5035 | 0.50373 | | |
| | | | 0.5035 | 0.50373 | | |
| | | | 0.3940 | 0.39400 | | |
| 7.7 N KI | 1.000 | 0.1006 | 0.3940 | 0.39400 | 0.0631 | 0.0578 |
| " | 1.000 | 0.01006 | 0.4571 | 0.45710 | | |
| | | | 0.4571 | 0.45710 | 0.0606 | |
| " | ... | 0.001006 | 0.5177 | 0.51770(?) | 0.0605 | 0.0582 |
| | | | 0.5176 | 0.51760(?) | | |
| 5.7 N KBr | 1.011 | 0.1006 | 0.3968 | 0.39652 | | |
| | | | 0.3968 | 0.39652 | 0.0606 | |
| " | 0.987 | 0.01006 | 0.4568 | 0.45714 | 0.0601 | 0.0578 |
| | | | 0.4563 | 0.45664 | | |
| " | ... | 0.001006 | 0.5166 | 0.51660(?) | 0.0601(?) | 0.0582 |
| | | | 0.5168 | 0.51680(?) | | |

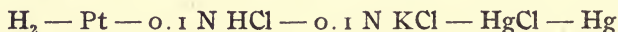
The results given in the above table indicate that potassium chloride is by far the most efficient of the salts used for eliminating contact potential. This conclusion is confirmed by some results obtained with the decinormal hydrochloric acid-calomel electrode.

Potential of H_2 —Pt—0.1 N HCl—0.1 N HCl—HgCl—Hg.—Two decinormal hydrochloric acid-calomel electrodes were prepared and measured against the hydrogen electrode in decinormal hydrochloric acid solution. The following corrected values were obtained for the electromotive force of the series

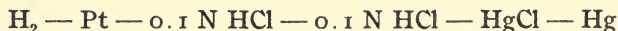


| Bar. pres. in ats. | E. M. F. | E. M. F. corr. for bar. press. |
|-----------------------|----------|-----------------------------------|
| 0.994 | 0.3999 | 0.40005 |
| 0.999 | 0.4003 | 0.40006 |
| 1.010 | 0.4005 | 0.40024 |
| Average | | 0.40012 |

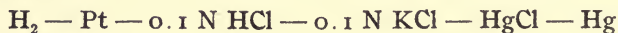
If we accept Lewis's conclusions that the potential of the 0.1 N HCl—HgCl—Hg electrode is the same as that of the 0.1 N KCl—HgCl—Hg electrode, then the difference between the electromotive force of the element



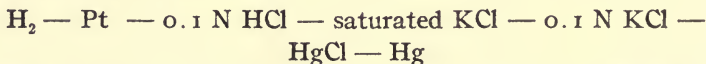
and that of the element



should be equal to the contact potential of the system 0.1 N HCl—0.1 N KCl. The actual difference which I find is $0.4266 - 0.4001 = 0.0265$. This value is very close to the difference which I find between the electromotive force of the element



and that of the element



viz., $0.4266 - 0.4000 = 0.0266$, the change in potential due to the presence of concentrated potassium chloride solution.

If, therefore, the assumption of Lewis in regard to the iden-

tity in potential of the hydrochloric acid and potassium chloride electrodes is granted, we reach the conclusion from the experiments with the hydrochloric acid electrode, as well as from those in which potassium chloride was used to eliminate contact potential, that *a saturated solution of potassium chloride eliminates almost completely the contact potential of liquid systems, at least those composed of potassium chloride-hydrochloric acid.*

It will be noticed, however, that the acceptance of the above assumption of Lewis also involves the acceptance of the value of 86 per cent. for the dissociation of 0.1 N hydrochloric acid. If this value is used the agreement of the figures obtained for the efficiency of potassium chloride for eliminating contact potential is by no means so good unless a corresponding decrease in the dissociation of the other concentrations of hydrochloric acid is assumed. Inasmuch as the value of 92.2 per cent. for the dissociation of 0.1 N hydrochloric acid is the value generally accepted, this is the value which has been used in calculating the potential of the calomel electrode, but the other values are also discussed.

It should be stated that the values obtained in the experiments involving the hydrochloric acid-calomel electrode are by no means as certain as those with the potassium chloride-calomel electrode, for the reason that only two acid electrodes were prepared. Work is now in progress on the HCl-HgCl-Hg and the $\text{H}_2\text{SO}_4\text{-Hg}_2\text{SO}_4\text{-Hg}$ electrodes.

Potential of the Decinormal Calomel Electrode

On the assumption that a concentrated solution of potassium chloride entirely eliminates the contact potential of the system 0.1 N HCl — 0.1 N KCl, the value of the electrode 0.1 N KCl-HgCl-Hg becomes $0.4000 - 0.0591 [-\log (0.1006 \times 0.922)] = 0.3390$. If the dissociation of 0.1 N hydrochloric acid is taken as 86 per cent., the corresponding value of the electrode becomes 0.3372. The value obtained by Sauer is 0.3406. If the contact potential of 0.1 N HCl — 0.1 N KCl is given the value 0.0284 assigned by Lewis, or 0.0286 found by Sauer, experimentally, and 86 per cent. is taken as the

degree of dissociation of 0.1 N hydrochloric acid, the value of the calomel electrode becomes 0.3355. It is evident that we cannot draw final conclusions until we know more accurately the per cent. of ionization of all the electrolytes concerned and have a very accurate method to calculate contact potential, and an experimental method to eliminate it completely. Such measurements of the electromotive force of various systems will perhaps be very helpful in this direction.

In the experiments in the following article the value 0.339 is used as the potential of the system 0.1 N KCl—HgCl—Hg, and the value 0.3355 is compared with this in the discussion.

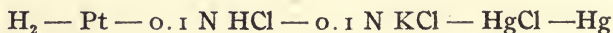
SUMMARY

This series of experiments has shown that:

1. Calomel electrodes, 0.1 N KCl—HgCl—Hg, can be prepared which for the first three weeks vary not more than 0.10 millivolt. With longer standing the variation slowly increases.

2. Platinum electrodes can be prepared which, when used as hydrogen electrodes in 0.1 N hydrochloric acid, show a variation from the mean value of less than 0.10 millivolt.

3. The electromotive force of the system



is 0.4266.

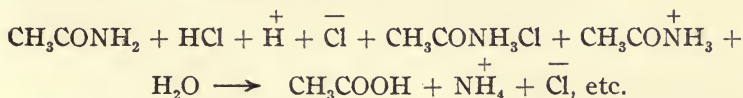
4. Saturated potassium chloride solution eliminates almost completely the contact potential of systems consisting of potassium chloride and hydrochloric acid.

5. The value of the potential of the electrode 0.1 N KCl—HgCl—Hg is 0.339 if the dissociation of 0.1 N hydrochloric acid is 92.2 per cent.; it is 0.337 if the dissociation of the acid is 86 per cent., and 0.3355 if the contact potential is assumed to be 0.0284. The results obtained by using these different values are discussed in the following article and are found to harmonize better with Lewis's data.

The Application of the Hydrogen Electrode to the Measurement of the Hydrolysis of Aniline Hydrochloride, and the Ionization of Acetic Acid in the Presence of Neutral Salts

We organic chemists have been nearly completely baffled in the study of some of our reactions because of the lack of some *direct, accurate and very rapid* method for determining the concentration of hydrogen ions (also hydroxyl, chloride, bromide, sulphide ions) in the presence of all organic compounds, especially when the system is undergoing change.¹ We have methods involving conductivity, catalysis, dilatation, colorimetry, etc., some or all of which can be applied reasonably well in some cases; but all of these methods may fail utterly in special cases, especially when the solution is constantly varying in composition.

When acetamide (or any ester, oxime, etc.) is hydrolyzed in the presence of hydrochloric acid a small amount of the salt of the amide is formed, and the concentration of this salt is constantly diminished as the amide disappears.



We have no method to-day for determining the concentrations of the constituents of such a system, as there are too many *unknowns* in the equation. If, however, we had a *direct, accurate, instantaneous method* for determining at any moment the concentration of the hydrogen ions, we could calculate the concentration of the amide salt and its ions, and could then determine directly whether this amide salt, or its ions, or some other constituent, is the substance directly

¹ See the address of the Chairman of the Division of Organic Chemistry in Section C of the American Association for the Advancement of Science, Baltimore, 1908. Science, 30, 624.

yielding the end products. We have the same case in the decomposition of amides, esters, etc., by alkalis, and just as great a need for a satisfactory method for determining the concentration of hydroxyl ions.

With these facts in mind, and with the advantage of the experiences of Desha¹ in this investigation, I have taken up again the attempt to apply the hydrogen electrode to this problem. In the present communication I am presenting some experiments bearing on the *accuracy of the hydrogen electrode* for determining the concentration of hydrogen ions in the presence of the organic substances aniline and acetic acid. I have chosen these simple compounds because the substances are stable, the constants which I wish to measure have been accurately determined by other methods, and I eliminate the uncertainties due to the changes in a reacting system. The question of the *rapidity* attainable in measuring the concentration of the hydrogen ions of a solution has been considered in an article by Desha and Acree. So many more unforeseen difficulties have beset me in this work with organic compounds than ever occur in work with inorganic substances that I shall present these difficulties rather fully for the benefit of others.

Hydrolysis of Aniline Hydrochloride

One of my first experiments to learn whether the hydrogen electrode might be applied to organic reactions was the determination of the hydrolysis of aniline hydrochloride.

The hydrolysis of this salt had been carefully determined by Bredig² by the conductivity method to be 2.63 per cent. at 25° in N/32 solution. Denham had applied the hydrogen electrode to this problem and determined the hydrolysis of aniline hydrochloride in N/16, N/24 and N/32 solutions. For the N/32 solution he obtained the value 2.58 per cent., a result agreeing remarkably well with the value determined by Bredig for the same solution. There are two small points in Denham's work, however, in which there is a chance for difference of opinion. In the first place the number 2.58 is

¹ Desha: Diss., Johns Hopkins Univ., 1909.

² Z. physik. Chem., **13**, 289 (1894).

not the percentage hydrolysis of the N/32 solution of aniline hydrochloride, but rather the ratio $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$. To obtain the degree of hydrolysis this value must be divided by 0.96, the degree of dissociation of N/32 hydrochloric acid. This raises the degree of hydrolysis to 2.69. The second point is a much more vital one. He uses the number 0.56 as the value of his normal calomel electrode. This value is the one determined by Rothmund by the drop-electrode method at 18°. Denham's measurements were carried out at 25°. If we apply the temperature factor of the normal calomel electrode as determined by Richards¹ we obtain for the potential of the electrode at 25° the value $0.56 + (7 \times 0.0006) = 0.564$. If this value is used in the calculations instead of 0.56, the ratio $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ for the N/32 solution is found to be 3.02 instead of 2.58, and the per cent. of hydrolysis becomes 3.15, a value differing quite widely from that obtained by Bredig.

Desha attempted to repeat the experiments of Denham, along with other experiments of his own, in this laboratory, but had little success. For the N/32 solution Desha found the ratio $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ to be 5.79. He was troubled chiefly by the decomposition of his material, the solution acquiring a pink color after the experiment had proceeded for a time.

The aniline hydrochloride prepared by Desha had not been recrystallized, whereas the material used by Denham was repeatedly recrystallized from acetone and finally washed with ether. Thinking that the cause of the discrepancies between the results of Denham and Desha might be due to impurities present in Desha's salt, I prepared my aniline hydrochloride with considerable care, especially as Dr. Denham had kindly told me of his own difficulties in this connection.

The aniline was fractionally distilled twice, the fraction boiling between 182° and 183° being used for the preparation of the hydrochloride. It was dissolved in ether and the hydrochloride precipitated by passing in dry hydrochloric acid

¹ Z. physik. Chem., 24, 53 (1897).

gas, the solution being kept cold by an ice bath. The white crystals were filtered off, washed repeatedly with ether and dried over sulphuric acid and caustic potash *in vacuo*. This formed Sample I.

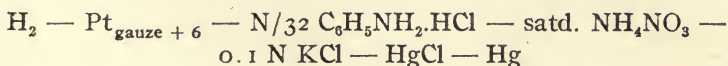
Of this dry salt 4.0478 grams were dissolved in 500 cc. of conductivity water to form a N/16 solution. A portion of this was diluted to form a N/32 solution.

The results obtained with these first two solutions are shown in the following table. In accordance with the practice of both Denham and Desha, saturated ammonium nitrate solution was used to eliminate the contact potential. The value of the calomel electrode used is 0.339.

| Concentration | E. M. F. Corrected for calomel electrode | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ |
|---------------|--|---|
| N/16 | 0.5066 | 2.30 |
| | 0.5003 | 2.95 |
| N/32 | 0.5124 | 3.68 |
| | 0.4943 | 7.47 |
| N/32 | 0.5072 | 4.51 |
| | 0.5064 | 4.64 |
| N/32 | 0.5129 | 3.61 |
| N/32 | Indefinite | |

As will be noted, the results are extremely discordant. Almost invariably the gauze electrode gave a higher value than the sheet electrode. To see if the electrodes were at fault, they were tested, after the first experiment, in a solution of 0.1 N hydrochloric acid, the electrodes having first been washed with alcohol and ether. Both electrodes gave the same potential, this fact showing that they were all right. It was noted in each of these experiments, after the removal of the electrodes, that there was oil on the surface of the solution. As no trouble of this kind was experienced with solutions of acids, it is probable that the oil was present at first in the aniline hydrochloride, or was the product of the decomposition of some substance present in the aniline hydrochloride solution. As in these experiments it had been the custom to have the sheet electrode partially out of the solution, the lower value of this electrode is probably due to its becoming coated with this oil. In subsequent experiments

the sheet electrode was entirely immersed, but in the other samples of aniline hydrochloride, which were further purified as described below, no traces of oil were found. No pink color, described by Desha, was noticed in the solution in any of the experiments. Constant readings were generally obtained in three hours, the drift being very small after the first hour and a half. A typical experiment with the N/32 solution is given below:



| Time | Electromotive force | |
|-------------|---------------------|--------|
| | 14 : gauze | 14 : 6 |
| 12.06 P. M. | Started | |
| 12.11 P. M. | 0.5021 | 0.4995 |
| 12.55 P. M. | 0.5058 | 0.5042 |
| 1.58 P. M. | 0.5067 | 0.5055 |
| 2.15 P. M. | 0.5067 | 0.5058 |
| 3.10 P. M. | 0.5070 | 0.5062 |

The remainder of the aniline hydrochloride was further purified by precipitating it from alcohol by the addition of ether. The material was filtered off and washed with ether to remove all traces of alcohol. The salt was dried *in vacuo* over solid caustic potash and sulphuric acid. This material constituted Sample II. The hydrolysis of N/16 and N/32 solutions of this salt was determined as before except that experiments were also performed with potassium chloride solution to eliminate the contact potential. The summary of the results is given in the following tables:

| Conc. | E. M. F. with NH_4NO_3 | | - E. M. F. with KCl | |
|-------|--|---|-----------------------------|---|
| | Corr. for calomel electrode | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ | Corr. for calomel electrode | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ |
| N/16 | 0.5005 | 2.92 | | |
| | 0.4999 | 2.99 | | |
| N/16 | 0.5009 | 2.88 | 0.5086 | 2.13 |
| | 0.5009 | 2.88 | 0.5095 | 2.06 |
| N/32 | 0.5126 | 3.63 | 0.5161 | (3.18) |
| | 0.5127 | 3.62 | 0.5168 | (3.10) |
| N/32 | | | 0.5189 | 2.86 |
| | | | 0.5190 | 2.85 |

The results obtained in the experiments in which potassium chloride was used to eliminate the contact potential agree much more closely with the results obtained by Bredig and by Denham than do those in which ammonium nitrate was used.

The remainder of the aniline hydrochloride was recrystallized from acetone and the product washed thoroughly with ether. After it was dried, solutions were prepared from this Sample III. Only potassium chloride was used in the contact solution with this sample. The results are summarized below:

| E. M. F. with KCl | | | | |
|-------------------|-----------------------|---|-------------------|--|
| Conc. | Bar. pres. in ats. | Corr. ¹ for calomel electrode | Corr. for bar. | $\frac{[H' \text{ conc.}] \times 100}{[\text{total sal}]}$ |
| N/16 | 1.011 | 0.5088 | 0.50852 | 2.15 |
| | | 0.5092 | 0.50892 | 2.11 |
| N/16 | 1.002 | 0.5091 | 0.50905 | 2.09 |
| | | 0.5089 | 0.50885 | 2.11 |
| N/32 | 1.011 | 0.5184 | 0.51812 | 2.94 |
| | | 0.5190 | 0.51872 | 2.85 |
| N/32 | 1.002 | 0.5184 | 0.51835 | 2.91 |
| | | 0.5184 | 0.51835 | 2.91 |

The agreement between the results of the two experiments at each concentration is very good in this series and furthermore the results agree well with those obtained with Sample II when potassium chloride was used in the contact solution, if the one experiment be excluded in which the values 3.18 and 3.10 were obtained for the N/32 solution.

A typical experiment in which potassium chloride is used in the contact solution is shown below:

$H_2 - Pt_{\text{gauze}} + 6 - N/16 C_6H_5NH_2.HCl \text{ (III)} - \text{satd. KCl} - 0.1 N$
 $KCl - HgCl - Hg \text{ (No. 14)}$

| Time | 14 : gauze | 14 : 6 | 6 : gauze |
|-------------|------------|--------|-----------|
| 8.42 A. M. | Started | | |
| 9.52 A. M. | 0.5088 | 0.5048 | |
| 10.13 A. M. | 0.5090 | 0.5072 | |
| 10.28 A. M. | 0.5090 | 0.5079 | |
| 10.58 A. M. | 0.5091 | 0.5085 | 0.00051 |
| 12.08 P. M. | 0.5091 | 0.5089 | 0.00017 |

¹ It is worthy of note that the averages of the electromotive force, and of the per cent. of hydrolysis, per cent. of ionization, and other factors depending upon the electromotive force, are approximately the same for long time periods whether corrected for the barometric pressure or not. The fluctuations of the barometer here in Baltimore are such that the pressure averages close to 760 mm. over long time periods.

A fresh lot of aniline hydrochloride was prepared and was extracted four times with about 200 cc. of boiling acetone. The material remaining was well washed with ether, dried, and used as Sample IV:

| Conc. | Bar. pres. in ats. | E. M. F. with KCl | | |
|-------|-----------------------|--------------------------------|-------------------|---|
| | | Corr. for calomel electrode | Corr. for bar. | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ |
| N/16 | 0.987 | 0.5087 | 0.50904 | 2.10 |
| | | 0.5083 | 0.50864 | 2.13 |
| N/16 | 0.989 | 0.5100 | 0.51028 | 1.9 |
| | | 0.5100 | 0.51028 | 1.99 |
| N/16 | 1.009 | 0.5103 | 0.51007 | 2.01 |
| | | 0.5100 | 0.50977 | 2.04 |
| N/32 | 0.996 | 0.5182 | 0.51830 | 2.93 |
| | | 0.5180 | 0.51810 | 2.95 |
| N/32 | 1.009 | 0.5180 | 0.51777 | 2.98 |
| | | 0.5179 | 0.51767 | 2.99 |

Sample V of the aniline hydrochloride was prepared by recrystallizing some of Sample IV from alcohol by the addition of ether. It gave the following results:

| Conc. | Bar. pres. in ats. | E. M. F. with KCl | | |
|-------|-----------------------|--------------------------------|-------------------|---|
| | | Corr. for calomel electrode | Corr. for bar. | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ |
| N/16 | 1.009 | 0.5098 | 0.50957 | 2.06 |
| | | 0.5098 | 0.50957 | 2.06 |
| N/16 | 0.996 | 0.5086 | 0.50870 | 2.13 |
| | | 0.5094 | 0.50950 | 2.06 |
| N/16 | 0.997 | 0.5102 | 0.51028 | 1.99 |
| | | 0.5097 | 0.50978 | 2.04 |
| N/32 | 0.988 | 0.5173 | 0.51761 | 3.01 |
| | | 0.5173 | 0.51761 | 3.01 |
| N/32 | 0.998 | 0.5177 | 0.51775 | 2.99 |
| | | 0.5177 | 0.51775 | 2.99 |
| N/32 | 0.999 | 0.5183 | 0.51832 | 2.93 |
| | | 0.5180 | 0.51802 | 2.96 |

Sample VI was prepared by recrystallizing the remaining material of Sample V from alcohol by the addition of ether. The results obtained with this material are given in the following table:

| Conc. | Bar. pres. in ats. | E. M. F. with KCl | | |
|-------|-----------------------|--------------------------------|-------------------|---|
| | | Corr. for calomel electrode | Corr. for bar. | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ |
| N/16 | 0.997 | 0.5096 | 0.50968 | 2.05 |
| | | 0.5092 | 0.50928 | 2.09 |
| N/16 | 0.995 | 0.5100 | 0.51013 | 2.01 |
| | | 0.5097 | 0.50983 | 2.04 |
| N/32 | 0.995 | 0.5189 | 0.51903 | 2.85 |
| | | 0.5187 | 0.51883 | 2.87 |
| N/32 | 1.003 | 0.5188 | 0.51872 | 2.88 |

A summary of the results obtained with the different samples of aniline hydrochloride when potassium chloride was used as the contact solution is given in the following table:

| <i>Aniline Hydrochloride</i> | | | | |
|------------------------------|------|---|-----------------------------|--|
| Sample | N/16 | $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ | Sample | N/32 $\frac{[H' \text{ conc.}] \times 100}{[\text{total salt}]}$ |
| II | | 2.13 | II | (3.18) |
| | | 2.06 | | (3.10) |
| III | | 2.15 | | 2.86 |
| | | 2.11 | | 2.85 |
| | | 2.09 | III | 2.94 |
| | | 2.11 | | 2.88 |
| IV | | 2.10 | | 2.91 |
| | | 2.13 | | 2.91 |
| | | 1.99 | IV | 2.93 |
| | | 1.99 | | 2.95 |
| | | 2.01 | | 2.98 |
| V | | 2.04 | | 2.99 |
| | | 2.06 | V | 3.01 |
| | | 2.06 | | 3.01 |
| | | 2.13 | | 2.99 |
| | | 2.06 | | 2.99 |
| VI | | 1.99 | | 2.93 |
| | | 2.04 | | 2.96 |
| | | 2.05 | VI | 2.85 |
| | | 2.09 | | 2.87 |
| | | 2.01 | | 2.88 |
| | | 2.04 | | |
| | | 2.07 | Average | 2.93 |
| | | 0.08 | Max. variation from mean | 0.08 |

Excluding the values in the parentheses, we have the average value of 2.07 for the N/16 solution and 2.93 for the N/32 solution. This gives us the following per cent. of hydrolysis of N/16 and N/32 solutions of aniline hydrochloride if we use 0.944 and 0.960 as the degree of ionization of N/16 and N/32 solutions of hydrochloric acid.

$2.07/0.944 = 2.19$ per cent. hydrolysis of N/16 aniline hydrochloride.

$2.93/0.960 = 3.05$ per cent. hydrolysis of N/32 aniline hydrochloride.



The per cent. of ionization of aniline hydrochloride can be calculated from conductivity data given by Bredig.¹ From these data the ionization of N/32 aniline hydrochloride is 86.6 per cent. and by extrapolation the ionization of the N/16 solution is found to be 84.4 per cent.

Let k_w = the ionization constant of water and k_b = the affinity constant of aniline.



$$\frac{k_w}{k_b} = \frac{C_{\text{C}_6\text{H}_5\text{NH}_2} C_{\text{H}^+}}{C_{\text{C}_6\text{H}_5\text{NH}_3^+}} = \frac{[\text{C}_{\text{H}^+}]^2}{C_{\text{C}_6\text{H}_5\text{NH}_3^+}}$$

$$\begin{aligned} C_{\text{C}_6\text{H}_5\text{NH}_3^+} &= C_{\text{C}_6\text{H}_5\text{NH}_3\text{Cl}} \times \text{ionization} \\ &= \frac{(1 - \text{per cent. hydrolysis}/100) \times \text{ionization}}{\text{volume}} \end{aligned}$$

$$\therefore \frac{k_w}{k_b} = \frac{[\text{C}_{\text{H}^+}]^2 \times \text{volume}}{(1 - \text{per cent. hydrolysis}/100) \times \text{ionization}}$$

For $V = 16$

$$\frac{k_w}{k_b} = \frac{(0.0207)^2}{(1 - 0.0219) \times 0.844 \times 16} = 0.0000324$$

For $V = 32$

$$\frac{k_w}{k_b} = \frac{(0.0293)^2}{(1 - 0.0305) \times 0.869 \times 32} = 0.0000318$$

Average value of $k_w/k_b = 0.321 \times 10^{-4}$

Tizard² obtained by colorimetric methods the value $0.242 \times$

¹ Z. physik. Chem., **13**, 191 (1894).

² J. Chem. Soc., **98**, 2492 (1910).

10^{-4} for k_w/k_b while Bredig found 0.24×10^{-4} by his conductivity measurements. Two factors enter into the explanation of the difference between these results. The first point is that Tizard assumes that the hydrochloric acid formed by the hydrolysis of the aniline hydrochloride is entirely dissociated. As was pointed out in the discussion of Denham's work, this assumption is not justifiable. The second factor has to do with the calculation of my results. It was pointed out in the discussion of Denham's work that the value assigned to the potential of the calomel electrode plays a large part in the value found for the hydrogen ion concentration. This indicates that the greatest source of uncertainty in the determination of the hydrolysis of aniline hydrochloride is not in any difficulty in the experimental measurements, as Desha thought, but in the determination of the potential of the calomel electrode. If the value of the decinormal calomel electrode is taken as 0.3362, the figure adopted by Desha, the ratio $[H' \text{ conc.}] \times 100 / [\text{total salt}]$ found for N/16 aniline hydrochloride becomes 1.85 instead of 2.07. If Lewis's value of the contact potential between 0.1 N potassium chloride and 0.1 N hydrochloric acid is adopted, viz., 0.0284, the value of the calomel electrode becomes 0.3355 and the ratio $[H' \text{ conc.}] \times 100 / [\text{total salt}]$ becomes 1.81 for the N/16 and 2.56 for the N/32 solution.

If these values are used

$$k_w/k_b \text{ for N/16} = 0.247 \times 10^{-4}$$

$$k_w/k_b \text{ for N/32} = 0.242 \times 10^{-4}$$

This gives an average of 0.244×10^{-4} for k_w/k_b , which agrees well with the values found by Tizard and Bredig. It should be noted that Bredig used the value 383 for the equivalent conductivity of the hydrochloric acid formed by hydrolysis of the aniline salt, whereas Lewis used 389.9. This makes no appreciable difference in k_w/k_b . Bredig's equivalent conductivity should change with change in concentration according to the isohydric principle. I intend to redetermine all the data needed for such work.

Experiments with Acetic Acid

To test the applicability of the hydrogen electrode to the determination of the concentration of the hydrogen ions in solutions containing weak organic acids, a series of experiments was carried out with acetic acid.

First, two experiments were carried out with 0.5 N acetic acid, with saturated ammonium nitrate as the contact solution.

$H_2 - Pt - 0.5 \text{ N } CH_3COOH - \text{satd. } NH_4NO_3 - 0.1 \text{ N } KCl -$
No. 14

This series gave the results:

| E. M. F. Corr. for calomel electrode | Per cent. dissocia- tion |
|--|--------------------------------|
| 0.4817 | 0.764 |
| 0.4822 | 0.748 |

With 0.25 N acetic acid and ammonium nitrate, the results were as follows:

| E. M. F. Corr. for calomel electrode | Per cent. dissociation |
|--|---------------------------|
| 0.4908 | 1.069 |
| 0.4905 | 1.081 |
| 0.4905 | 1.081 |

With 0.25 N acetic acid and potassium chloride as contact solution, the results were the following:

| E. M. F. Corr. for calomel electrode | Per cent. dissociation |
|--|---------------------------|
| 0.4930 | 0.982 |
| 0.4927 | 0.993 |

The difference of approximately 0.1 between the per cent. of ionization determined with ammonium nitrate and that determined with potassium chloride is evidently due to the change in contact potential in the two systems. Judging from the previously described experiments with potassium chloride, that solution is the better for eliminating contact potential and therefore the per cent. ionization of 0.25 N

acetic acid is probably nearer 0.985 than 1.080. By conductivity measurements White and Jones¹ found at 25° the dissociation of 0.5 N acetic acid to be 0.58 and of 0.25 N acetic acid to be 0.89 (calculated by interpolation).

Effect of Neutral Salts upon the Dissociation of Acetic Acid.—The catalytic action of neutral salts is a problem upon which a great deal of work has been done. The literature of this field and the principal theories have been summarized by Acree.² Besides the catalytic action of neutral salts upon the velocity of decomposition of diacetone alcohol by alkalis, cane sugar inversion, etc., work has been done upon the effect of neutral salts on the dissociation of weak acids. In the study of this problem two methods have been used heretofore. The conductivity method has been applied by Arrhenius³ and the colorimetric method by Brunel and Acree⁴ and by Szyszkowski.⁵ Arrhenius studied the conductivity of acetic, formic and phosphoric acids in the presence of a number of different salts. He came to the conclusion that the effect of small quantities of neutral salts upon the dissociation of the acids is much greater at the higher dilutions of the acids than at the lower; whereas if the amount of salt added is larger, the effect is nearly proportional to the amount of salt added. The addition of 0.125 N sodium chloride and 0.5 N acetic acid increased the hydrogen ion concentration by 5 per cent. A number of factors enter into conductivity measurements which make these results uncertain. Among these factors are the change in hydration and in viscosity caused by the salt; the possibility of double compounds or complex ions between the salt and acid; the relatively small change in conductivity due to any change in the hydrogen ion concentration compared to the conductivity of the salt added; and other factors.

Szyszkowski based his method upon the change in color of methyl orange in the presence of weak acids caused by the addition of neutral salts. He studied acetic and carbonic

¹ *Am. Chem. J.*, **44**, 159 (1910).

² *Ibid.*, **41**, 457 (1909).

³ *Z. physik. Chem.*, **1**, 110; **11**, 823; **31**, 197 (1899).

⁴ *Am. Chem. J.*, **36**, 120 (1906).

⁵ *Z. physik. Chem.*, **58**, 420 (1907); **63**, 421 (1908); **73**, 269 (1910).

acids, using solutions varying from 0.0022 N to 0.046 N. He interpreted his results to mean that neutral salts greatly increase the hydrogen ion concentration of weak acids. Sodium chloride apparently increased the ionization of acetic acid about 23 times. It should be pointed out, however, that Kurt Meyer and also Hantzsch have shown that some dyes unite with salts and form still more deeply colored double compounds. This tends to throw doubt on the validity of Szyszkowski's conclusions until further evidence to the contrary is presented.

It was believed that the hydrogen electrode would prove serviceable in the study of this problem, and to that end a series of experiments was performed.

In order that the effects of potassium chloride and ammonium nitrate for eliminating contact potential might be compared, each solution of acetic acid was used with both contact solutions. The results are included in the following table: The solutions were prepared by mixing 0.5 N acetic acid with an equal volume of the different solutions of potassium chloride. The concentrations given below are the concentrations after mixing the two solutions. To make the table complete the results obtained with 0.25 N acetic acid alone are included. Only the corrected electromotive force readings are given:

| Solution | NH ₄ NO ₃ as contact soln. | | KCl as contact soln. | |
|-------------------------------|--|---------|-------------------------------|---------|
| | E. M. F. corr. for bar. | Dissoc. | E. M. F. corr. for bar. | Dissoc. |
| 0.25 N Acetic | 0.49032 | 1.089 | 0.49308 | 0.980 |
| | 0.49071 | 1.073 | 0.49296 | 0.980 |
| | 0.49071 | 1.073 | | |
| 0.25 N Acetic + 0.05 N KCl | 0.49152 | 1.041 | 0.49276 | 0.990 |
| | 0.49192 | 1.026 | | |
| 0.25 N Acetic + 0.1 N KCl | 0.49271 | 0.992 | 0.49178 | 1.030 |
| | 0.49271 | 0.992 | 0.49178 | 1.030 |
| 0.25 N Acetic + 0.5 N KCl | 0.49445 | 0.925 | 0.48945 | 1.125 |
| | 0.49445 | 0.925 | 0.48945 | 1.125 |
| 0.25 N Acetic + 2.06 N KCl | 0.49837 | 0.797 | 0.48575 | 1.300 |
| | 0.49837 | 0.797 | 0.48575 | 1.300 |

The results of this series of experiments are uncertain. According to the experiments with ammonium nitrate, the addition of a neutral salt appears to decrease the hydrogen ion concentration; according to the experiments with potassium chloride, the hydrogen ion concentration appears to increase. The difficulty evidently lies in the contact potential of the system. I tried to carry out some experiments in which ammonium nitrate was added to acetic acid, but these were unsuccessful for some reason. Instead of the potential becoming constant within about two hours it would continue to rise, showing a decrease in the hydrogen ion concentration of the solution. This may be due to a reduction of the ammonium nitrate to ammonia by the hydrogen in the presence of platinum black.

If we assume the potassium chloride series of results to be the more accurate, as they have been seen to be in other experiments, then the results are not dissimilar to those obtained by Arrhenius. The addition of 0.1 N potassium chloride to 0.25 N acetic acid increases the hydrogen ion concentration about 4.5 per cent. of the original value. I shall extend this study in several related directions.

SUMMARY

1. If we use 0.339 as the value of the electrode 0.1 N KCl—HgCl—Hg, the hydrolysis of a N/16 solution of aniline hydrochloride is 2.19 per cent. while that of the N/32 solution is 3.05 per cent. If we use 0.3355, calculated from the data of Lewis, as the value of this electrode the hydrolysis becomes 1.81 per cent. for the N/16 and 2.56 per cent. for the N/32 solutions, values which agree excellently with those of Bredig and Tizard. The hydrogen electrode gives us then another instrument for studying these relations between conductivity and hydrolysis accurately, and we shall extend these studies to a large number of other organic salts.

2. The addition of potassium chloride to acetic acid solutions slightly increases the dissociation of the acetic acid.

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BIOGRAPHY.

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